TECHNICAL AND ECONOMIC ASSESSMENT OF THE APPLICATION OF MEMBRANE TECHNOLOGY FOR TREATING OIL/WATER/MINERAL EMULSIONS

FINAL REPORT

VOLUME I - LITERATURE REVIEW

Report Prepared for

CANMET/ERL

Department of Energy, Mines, and Resources, Canada

Contract No. OSQ83-00203 23.9185

by

JUL 03 1995

ZENON ENVIRONMENTAL INC.

MICROMEDIA

96 pp

April 22, 1985

TABLE OF CONTENTS

	Page No.
1.0 **INTRODUCTION**	1-1
2.0 **OVERVIEW OF PRODUCED WATER TREATMENT PRACTICES**	2-1
2.1 PRODUCED WATER CHARACTERISTICS	2-1
2.1.1 PRODUCED WATER QUALITY	2-1
2.1.1.1 OIL/WATER/MINERAL EMULSIONS	2-2
2.1.1.2 INORGANIC CONSTITUENTS	2-4
2.1.1.3 ORGANIC CONSTANTS	2-4
2.1.2 PRODUCED WATER QUANTITY	2-7
2.2 TREATMENT REQUIREMENTS	2-10
2.2.1 OIL REMOVAL	2-11
2.2.2 BOILER FEEDWATER REQUIREMENTS	2-13
2.3 TREATMENT OF OIL/WATER/MINERAL EMULSIONS	2-17
2.3.1 EXISTING TECHNOLOGIES	2-17
2.3.1.1 DESIGN	2-17
2.3.1.2 ECONOMIC EVALUATION	2-21
2.3.1.3 TECHNICAL EVALUATION	2-23
2.3.2 EMERGING TECHNOLOGIES	2-28
2.4 PREPARATION FOR USE AS BOILER FEEDWATER	2-32
2.4.1 EXISTING TECHNOLOGIES	2-32
2.4.1.1 DESIGN	2-32
2.4.1.2 ECONOMIC EVALUATION	2-39
2.4.1.3 TECHNICAL EVALUATION	2-39

TABLE OF CONTENTS (Cont'd)

	Page No.
2.4.2 EMERGING TECHNOLOGIES	2-41
3.0 APPLICATION OF MEMBRANE TECHNOLOGIES FOR TREATMENT OF PRODUCED WATER	3-1
3.1 BACKGROUND	3-1
3.2 TREATMENT OF OIL/WATER/MINERAL EMULSIONS BY ULTRAFILTRATION	3-3
3.2.1 PROCESS DESCRIPTION	3-3
3.2.1.1 MEMBRANE MATERIALS	3-6
3.2.1.2 CONFIGURATIONS	3-10
3.2.2 CURRENT APPLICATIONS AND ECONOMIC EVALUATION	3-16
3.2.3 APPLICATIONS IN THE OILFIELD	3-21
3.3 PREPARATION OF BOILER FEEDWATER BY REVERSE OSMOSIS	3-24
3.3.1 PROCESS DESCRIPTION	3-24
3.3.1.1 MEMBRANE MATERIALS	3-27
3.3.1.2 CONFIGURATIONS	3-29
3.3.2 CURRENT APPLICATIONS AND ECONOMIC EVALUATION	3-30
3.3.3 APPLICATIONS IN THE OILFIELD	3-35
3.4 POTENTIAL UF/RO MEMBRANE SYSTEM DESIGN	3-36

TABLE OF CONTENTS (Cont'd)

	Page No.
4.0 RECOMMENDED MEMBRANES	4-1
4.1 RECOMMENDED MEMBRANES	4-1
4.2 EXPERIMENTAL PROCEDURES	4-2
REFERENCES	R-1

LIST OF FIGURES

Figure No.		Page No.
2-1	Structure of Petroleum Acid Emusion Stabilizers	2-3
2-2	Process Schematic for Treatment of Produced Water to Once-Through Steam Generator Feedwater Quality	2-20
2-3	Water Treatment Process at Kern River	2-34
2-4	Unit Removal Efficiencies at Kern River	2-34
2-5	Process Schematic for Recycle of Produced Water from Cyclic Steam Stimulation Bitumen Recovery at Cold Lake	2-36
2-6	Potential Water Re-Use Schemes	2-37
3-1	Membrane Ultrafiltration Process	3-4
3-2	Membrane Configurations	3-13
3-3	Reverse Osmosis	3-25
3-4	Process Schematic for RO Treatment System on High TDS Feedwater	3-32
3-5	Pre and Post Treatment Options on a UF/RO System for Treatment of Produced Water	3-37
4-1	Procedure for Membrane and Process Evaluations	4-3

LIST OF TABLES

Table No.		Page No.
2-1	A Survey of Major Components in Produced Water from Steam Stimulation Projects	2-5
2-2	Water Balance at Cold Lake	2-8
2-3	Water Production Forecast for Future Steamflood and Fireflood Operations	2-9
2-4	Water Quality Requiredments for Boiler Feedwater Preparation and Other Uses	2-12
2-5	Guidelines for Water Quality in Modern Industrial Water Tube Boilers for Reliable Continuous Operation	2-16
2-6	Capital and Operating Costs of Conventional Once-Through and Thermosludge Boilers	2-22
2-7	Unit Operation Assessment of Current Technologies	2-24
2-8	Assessment of Potential Water Reuse Schemes Evaluated for Cold Lake	2-38
3-1	Suitability of Process	3-2
3-2	Commerical Ultrafiltration Membranes	3-7
3-3	Typical Operating Limitations of Some Hydrophilic Ultrafiltration Membranes	3-11
3-4	Comparison of Membrane Configurations	3-15
3-5	Survey Results - Oily Wastewater Treatment System Annual Cost Summary	3-18
3-6	Estimated Cost Analyses at Alcoa Pennsylvania	3-20
3-7	Commercial Reverse Osmosis Membrane	3-28

1.0 INTRODUCTION

The total Canadian reserves of heavy oil and oil sands were estimated in 1979 to be 469 billion m^3 (Meyer and Dietzman, 1979), well in excess of the conventional oil reserves. In the coming years production of conventional oil is expected to remain static or decline, while production of bitumen from the non-conventional reserves is expected to increase.

The processes most commonly utilized to recover this resource are thermal processes involving steam injection, which require large volumes of water for steam generation. Depending on the production techniques utilized each barrel of bitumen brought to the surface may be associated with 2 to 10 barrels of water. Since recovery operations in Western Canada are located in water-short or environmentally sensitive areas, effort has been directed in recent years to the development of efficient and economic processes for the recycling of the produced water for treatment and reuse as boiler feedwater.

Several recovery operations are currently recycling the produced water using various combinations of conventional treatment units. To meet boiler feedwater requirements the removal of oil is required, along with hardness and suspended solids removal and silica reduction. One unique characteristic of the produced water from heavy oil/bitumen recovery operations is the frequent occurrence of highly stable oil/water emulsions. The treatment requirements for such emulsions are unique to oil field operations, and concerns have been expressed regarding the reliability, efficiency, and economy of current systems used to break these oil/water emulsions and produce

acceptable boiler feedwaters. The need for the development of the efficient and cost-effective recycling technology has been identified by the oil industry. Various alternative treatment and steam generation systems have been investigated to meet this objective. One potential solution to current problems is the application of ultrafiltration and/or reverse osmosis membrane processes for oil recovery and boiler feedwater preparation.

This study was undertaken to provide a technical and economic assessment of membrane technology for treatment of the stable oil/water/mineral emulsions produced during in-situ recovery operations.

Volume I of this report presents the results of a literature review undertaken to review and evaluate the technical efficiency and economics of conventional treatment systems currently employed and assess the potential for membrane applications to meet treatment requirements. Volume II contains the results of an experimental program conducted in order to determine the technical and economic feasibility of the application of membrane technology to emulsion treatment. Volume III contains the Appendices to the report.

To further the literature review appropriate public and private research centers active in oil recovery and membrane research were contacted, and the commercial literature of manufacturers and vendors was examined. Current treatment technologies are discussed, and related industrial applications of membrane systems are assessed. The potential of utilizing ultrafiltration for oil recovery, and reverse osmosis to meet remaining feedwater objectives is discussed.

2.0 OVERVIEW OF PRODUCED WATER TREATMENT PRACTICES

2.1 Produced Water Characteristics

In recent years, thermal or steam stimulation techniques have been implemented in the recovery of heavy oil/bitumen that is too viscous to flow at normal reservoir temperatures. These in-situ recovery schemes involve heating the oil to lower viscosity and initiate flow. The most common process is the so-called "huff and puff" method which involves intermittent steam injection. Steam flooding, which uses continuous steam injection has been employed as well. Other techniques under investigation include the "combination of forward combustion and water flood" (COFCAW) methods, and combinations of steam and fireflood methods. The formation water and condensed steam which is produced along with the oil, after initial phase separation, is referred to as produced water. Often this water occurs as part of a stable oil/water/mineral emulsion from in-situ recovery operations.

For the purposes of this report "produced water", will refer to the water remaining after separation of free oil. Produced water typically contains emulsified oil, suspended solids, dissolved organics and various inorganic components.

2.1.1 Produced Water Quality

Variations in produced water quality and quantity have been observed between wells and project, as well as over the life of an operation. In steam stimulation, which is a cyclic process, water quality is typically best in the early stages of the production cycle, and deteriorates torward the latter stages. Similarly, poorer water

quality in terms of TDS, silica, and hardness is typically observed in subsequent production cycles on the same well (CH_2M Hill, 1982).

The temperature of produced water, which is a consideration in the treatment process, is typically in the range of 65-82°C (150-180°F).

2.1.1.1 Oil/Water/Mineral Emulsions

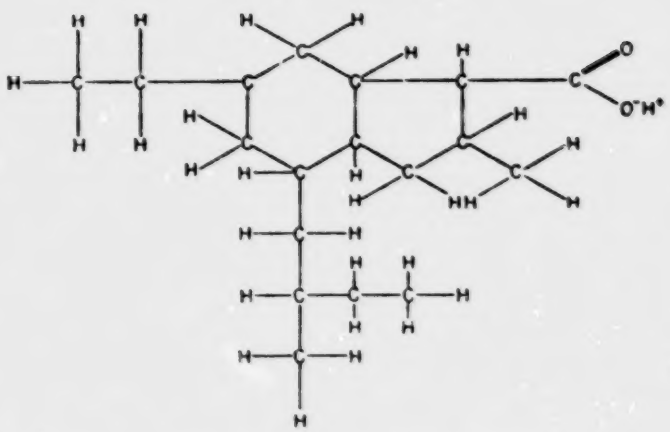
The oil/water/mineral emulsions associated with the production of heavy oil or bitumen are characterized by their unusual stability.

Gewers (1968) investigated the composition of stable heavy oil/bitumen emulsions and found that clay colloids and asphaltenes formed membranous skins which created highly stable emulsions. Conventional de-emulsifying processes, such as use of surface active compounds or electrostatic coalescence were ineffective on clay stabilized emulsions. Gewers found these emulsions to have minimum stability in the pH range of 7 to 9. He also found that the emulsions stabilized by asphaltanic skins are treatable with relatively high concentrations of water soluble surface - active compounds. Typical Alberta heavy oils contain approximately 20 per cent asphaltenes, compared with 2 per cent in conventional light crude. Petroleum acids, such as carboxylic and phenolic acids, can react with caustic soda which is injected to promote recovery, and can result in the formation of surface active chemicals which also promote emulsion stabilization. Figure 2-1 presents the molecular structure of carboxylic and (naphthenic) phenolic acids. Since these are polar compounds, their solubility in water may be a function of pH.

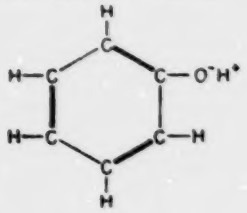
FIGURE 2-1

STRUCTURE OF PETROLIUM ACID EMULSION STABILIZERS
(from Gewer, 1968)

CARBOXYLIC ACID
(napthenic acid)



PHENOLIC ACID



Emulsified oil concentration varies as process conditions change and also varies between fields. At the Cold Lake project for example the emulsified oil in the water after conventional gravity separation normally ranges from about 50 to 400 mg/L. During conditions of treater upset, this level may go as high as 16,000 mg/L (Whalley and Wilson, 1979). Typical suspended oil concentrations in produced waters are reported to range from 100 to 2000 mg/L (CH_2M Hill, 1982).

2.1.1.2 Inorganic Constituents

The inorganic composition of produced water varies significantly between each oil recovery project. Table 2-1 summarizes the major components of produced water from several different pilot studies, and serves to illustrate this variability. A recent survey of heavy oil/oil sand operations in Western Canada (CH_2M Hill, 1982) reported the following range of inorganic constituents:

Total hardness	140-720 mg/L as $CaCO_3$
Silica	100-250 mg/L
Total dissolved solids	6,000-15,000 mg/L
Suspended solids	70-1,000 mg/L
Iron	0.1-0.8 mg/L

2.1.1.3 Organic Constituents

A detailed assessment of organic composition, especially dissolved organics, is not customary for once-through boiler feedwater preparation, and little information is available regarding effects of organics on oil recovery or boiler feed-water preparation. It is

TABLE 2 - 1

A SURVEY OF MAJOR COMPONENTS IN PRODUCED WATER FROM STEAM STIMULATION PROJECTS
(CH_2M - Hill, 1981)

Parameter	Esso Cold Lake Alberta	Suncor Ft. Kent Alberta	BP Marguerite Lake Alberta	Shell Peace River Alberta		Getty Oil Kern. River California	Texaco San Ardo California	Mobil S. Belridge California	Oil McKittrick California	Cat Canyon Field California
				Cold Prod.	Hot Prod.					
Ca (mg/L)	48	290	100	48	156	-	-	188	109	-
Mg (mg/L)	5	40	30	143		-	-	27	56	-
Na (mg/L)	1743	4 500	2500	11 007	2 252	215	2105	3 300	2500	1600
Total Hardness (mg/L $CaCO_3$)	141	890	374	709	-	132	162	580	503	41
CO_3 (mg/L)	15	0	0	300	0	15	0	-	45	0
HCO_3 (mg/L)	304	410	275	6 468	1 558	292	255	-	883	1281
SO_4 (mg/L)	111	525	175	22	379	53	410	-	180	150
Cl (mg/L)	3094	7 253	3850	13 348	2 569	199	2980	4 800	3517	788
S (mg/L)	40	0.01	-	-	-	0	10	-	0	-
NO_3 (mg/L)	-	0.34	-	-	-	0	-	-	-	-
B (mg/L)	10	-	-	-	-	1	-	-	15	-
SiO_2 (mg/L)	250	236	-	8	98	125	130	380	121	178
Fe (mg/L)	0.8	0.1	-	0.3	< 0.1	0.1	1.0	-	-	0.3
TDS (mg/L)	6015	13 300	7300	31 349	7 009	844	6115	13 000	7 000	3 132
pH	8.0	8.1	7.0	8.6	7.1	8.3	6.8	7.2	-	8.2
Conductivity (μmhos/cm)	-	17 000	-	50 000	11 100	1190	-	17 000	8360	4317
Suspended Solids (mg/L)	68	447	-	-		-	69	-	-	130
Oil (mg/L) (Insoluble or suspended oil)	400-2000	220	-	-		200	96	140	-	-

known that the reaction of steam and hot water with bitumen can lead to the formation of water soluble polar organics, and that process chemicals or humic substances may be present in the produced water (Burchfield and Hepler, 1979). Any dissolved substances, including dissolved organics, may be of importance in the recycling or treatment of such water for steam generation under the high pressure conditions commonly utilized. While Table 2-1 does not specify the dissolved organic constituents in the produced waters, it is interesting to note that several publications (Whalley and Wilson, 1979; Imperial Oil, 1978) have given the TOC as >30 mg/L in Cold Lake produced water before treatment. In the case of fireflooding or combustion waters, the TOC before treatment can be near 10,000 mg/L (Barbour and Guffey, 1979).

Produced water from steam stimulation studies at Esso's Leming Cold Lake Area pilot project was analyzed by Tsui and McCort (1979). The analyses of water samples obtained by these researchers were similar to the values shown for Cold Lake in Table 2-1. In addition, they determined NH_3 and phenol concentrations to be in the ranges of 10 to 22 mg/L and 11 to 38 mg/L, respectively. Tsui and McCort also found that, in general, produced water was more toxic to fish than petroleum refinery wastewater or mine depressurization groundwater from the Fort McMurray tar sands area.

A more recent study utilized TOC measurements and GC/MS analysis to identify the organics present in the produced water from two recovery operations in Alberta (ZENON, 1983). The TOC in one sample was appreciable at 583 mg/L. Characterization of the individual trace components in this sample found that in general lower

molecular weight substances predominate (<200 a.m.u.), particularly phenol and its alkylated congeners which where present at ppm levels. Also present in lower quantities were benzathiazole, naphthalene and dimethylibenzaldehydes. Variability between sites was found, as the organic content at the second site indicated similar phenol levels, although alkylated phenols and dimethylbenzaldehydes were much lower, while benzathiozole was not detected. Alkylated benzenes were found only in the second site. The study also investigated the effectiveness of various treatment techniques for TOC and trace organic removal. The TOC retentions on DP-1 resin, carbon, and XAD-2 resin were found to be negligible, 40%, and 18%, respectively.

2.1.2 Produced Water Quantity

Thermal recovery operations require large volumes of fresh water for steam generation. Table 2-2 illustrates the water balance at Cold Lake as an example of water requirements at in-situ operation. Total water requirements are in the order of 143,000 m^3/d, of which 35% is to be obtained by recycle.

The ratios of water to oil produced at the Cold Lake Area of Alberta are typically in the area of 2:1. Ratios as high as 10:1 have been reported from some areas of California (CH_2M Hill, 1982). In Canada, water-to-oil ratios are expected to increase with time and forecasters estimate that average water-to-oil and steam-to-oil ratios will increase from about 4:1 in 1984 to 6:1 in the year 2000. The trend, along with projected water quantities produced by year, is illustrated in Table 2-3. Water-to-oil ratios in conventional heavy oil recovery processes also vary between fields, and have been

TABLE 2 - 2

WATER BALANCE AT COLD LAKE (Imperial Oil, 1978)

Water Requirements	10^3 m^3/d
Injection Steam	63.6
Process Water and Steam	19.7
Cooling Tower	25.8
Water Treatment Backwash	17.6
Utility Water	12.7
Potable Water	3.8
Total	143.2
Consumed in Operations	
Displacing Bitumen	25.4
Cooling Tower Evaporation	20.0
Hydrogen Synthesis	2.4
Coke Gasification	5.1
Subtotal	52.9
Waste Disposal	
Deep Wells -	
Water Treatment Backwash	7.6
Sour Water	2.4
Desalter Brine	2.4
Chemical Wastes	0.8
Subtotal	13.2
Surface -	
Water Treatment Backwash	10.0
Cooling Tower Blowdown	3.3
Boiler Blowdown	2.7
Utility Water Waste	10.7
Subtotal	26.7
Recycled	
Produced Water	38.2
Sour Water	4.4
Sanitary Wastes	3.8
Oily Wastes	4.0
Subtotal	50.4
Total	143.2
Water Supply	
Recycled Water	50.4
Fresh Water Make-up	92.8
Total	143.2

TABLE 2 - 3

(ZENON, 1983)

WATER PRODUCTION FORECAST FOR FUTURE STEAMFLOOD AND FIREFLOOD OPERATIONS (Cold Lake, Peace River and Wabasca)

	Steam Huff & Puff*		Steamflood**		Fireflood**	
Year	Steam-to-Oil Ratio	Water (10^3 m^3/d)	Water-to Oil Ratio	Water (10^3 m^3/d)	Water-to Oil Ratio	Water (10^3 m^3/d)
1981	4	8.0	-	-	-	-
1982	4	12.0	-	-	-	-
1983	4	16.0	-	-	-	-
1984	4	16.0	4	4	-	-
1985	4	16.0	4	16	4	16
1986	5	20.0	4	16	3	12
1987	5	20.0	4	16	2	12
1988	5	20.0	4	30	2	15
1989	5	20.0	4	30	2	15
1990	5	20.0	5	37.5	2	15
1991	6	24.0	5	37.5	2	15
1992	6	24.0	5	37.5	2	15
1993	6	24.0	5	37.5	3	22.5
1994	6	24.0	5	37.5	3	22.5
1995	6	24.0	5	37.5	3	22.5
1996	6	24.0	6	45.0	3	22.5
1997	6	24.0	6	45.0	3	22.5
1998	6	24.0	6	45.0	3	22.5
1999	6	24.0	6	45.0	4	30.0
2000	6	24.0	6	45.0	4	30.0

* Steam huff & puff contributes a maximum of 4 x 10^3 m^3/d oil production.

** Steam-to-oil and water-to-oil ratios and trends based on arbitrary estimate and experience.

reported to range from a low of 0.3 to a high of 9.0 (ZENON, 1983). The expected increase in water production with time illustrates the attractiveness of efficient and economical recycling processes, which would eliminate problems associated with obtaining a source of water for steam generation, as well as disposal of unused produced water. Plants recycling water may only partially recycle the produced water, partially recycle and combine the water with other waste streams, or may recycle all the water and supplement with additional water. Thus quantities of produced water to be treated depend on the treatment requirements and process selected at a particular plant.

2.2 Treatment Requirements

The treatment requirements depend on the operating pressure and type of steam generation system used. Operating pressures vary between fields, and reported values range from 700 to 2400 psi (4830-16560 kPa). In the Cold Lake area of Alberta injection pressures typically range from 1200-2000 psi (8280 to 13800 kPa). Generally, higher pressure boilers demand higher quality feedwater. In all water reuse schemes, the type of boiler chosen ultimately determines the cost and complexity of the water treatment required. At the present time, most in-situ pilot or commercial plants use the conventional once-through oilfield steam generators which produce 80% quality steam and require relatively low quality feedwater. A recent survey of steam generation techniques which may utilize produced water found that economics at the present time still favoured the use of these generators (CH_2M Hill, 1982). Treatment requirements are dictated by

the need to maximize oil recovery and achieve acceptable boiler feedwater quality for any water being recycled (CH_2M Hill, 1981).

Table 2-4 presents general oilfield requirements for boiler feed water and other uses as obtained from the literature.

To treat produced water for use as once-through boiler feedwater, essentially all oil, hardness and suspended solids must be removed, and a reduction in silica is often required. The removal requirement for Total Dissolved Solids (TDS) varies depending on initial produced water concentration, since levels between fields may vary from less than 1,000 mg/L to over 30,000 mg/L.

In those water treatment schemes in which the produced water is only partially recycled, the remainder is often used for either backwashing filters and softeners or other miscellaneous uses (Stephenson et. al., 1983). Some waste streams which are unsuitable for reuse may be destined for surface or deep well disposal, but environmental regulations still require some degree of treatment for this (Table 2-4). In the event of boiler shutdown, it may be necessary to provide alternate water disposal means, thus unit operations should ideally be able to meet surface disposal guidelines as well.

2.2.1 Oil Removal

The American Boiler Manufacturers Association guidelines recommend oil removal to levels of 7 mg/L or less, with a desirable level being less than 1 mg/L. Oil in concentrations above this can cause scale adherence, film boiling, and coking in the boiler, and

TABLE 2 - 4

WATER QUALITY REQUIREMENTS FOR BOILER FEEDWATER PREPARATION AND OTHER USES
(from CH_2M Hill, 1981)

Parameter	Once-Through Steam Generator Note 4	Thermosludge Generator Note 4	Deep Well Disposal-Note 1	Irrigation	Cooling Water Make-up
Total Hardness mg/L as $CaCO_3$	< 0.5	100-2000			NOTE 2
Silica mg/L	< 50	10-250			NOTE 2
Oil mg/L	< 1	50-1000	< 20	< 5	< 1
TDS mg/L	< 8000	1000-50000		< 1000	-
Suspended Solids mg/L	0	10-500	< 5		NOTE 3
Dissolved O_2 mg/L	< 0.04	-			-
Iron	< 0.05				

NOTE 1 - Water should be chemically compatible with formation waters.

NOTE 2 - The product of Mg as $CaCO_3$ x SiO_2 < 35000 mg/L.

The product of Ca as $CaCO_3$ x SO_4 < 500,000 mg/L.

NOTE 3 - Total suspended solids in the recirculating water 200 mg/L.

NOTE 4 - These are vendor recommendations. Some of these values have been exceeded in actual practice.

fouling of ion exchange (softener) resins in the feedwater treatment train.

2.2.2 Boiler Feedwater Requirements

The most common causes of boiler scale are the presence of calcium and magnesium ions. With increasing temperature, the salts of these ions show a decreasing solubility. As a result, most guidelines recommend the removal of hardness to levels of less than 1 mg/L.

Control of silica in process waters is important, since amorphous collidal silica can form glass-like deposits on heat exchange surfaces. In the boiler silica can also produce scaling as a constituent of various complex mineral scales. Silica is not as great a problem in oilfield steam generators as in utility-type boilers, and control may consist of maintaining silica solubility by ensuring that alkalinity is at least 3 times the silica content (but less than 2,000 mg/L), or by careful control of residual calcium levels in feedwater. Operations have been reported with silica levels as high as 150 mg/L (Carrell, 1979).

Oil-field steam generators can tolerate a relatively high level of dissolved solids; their level becomes a concern only when liquid phase concentrations approach solubility limits. Therefore in 80% quality steam generation, feedwater salt concentrations close to 20% of their solubility limits should be possible. Thus sodium chloride levels of up to 50,000 mg/L may be tolerated. Permissible levels of feedwater TDS are generally dependent upon the limitations of the ion exchange softening systems commonly used. Most softeners utilize salt regenerated, strong acid resins whose hardness leakage

characteristics limit feedwater concentrations to between 5,000 and 7,000 mg/L. Weak acid resins have been recently applied, and have been reported to operate successfully at 28,000 mg/L, however costs are much higher. The maximum TDS concentration reported in oil-field steam generator blowdown, or condensate film fraction, are 125,000 to 150,000 mg/L (CH_2M Hill, 1982). Practical limits of TDS have been estimated as 40,000 mg/L in the feedwater, and 200,000 mg/L in condensate film.

Suspended solids contribute to softener fouling and boiler sludge formation, and as well they may contribute components in the formation of complex mineral scales. It is therefore critical that boiler feedwater should be essentially free of suspended solids.

Iron should be removed from boiler feedwater due to the possibility of the formation of corrosion products within the generator. Treatment for control of sulfide, oxygen, and pH are also essential to minimize corrosion and to allow successful boiler and equipment operation.

The pH of boiler feedwater must be maintained within the alkaline range, with optimum given as between 8 and 9, to a maximum of 12. These levels will promote silica solubility while also minimizing corrosion. Higher pressure operations generally require a pH of around 10.5 for maximum silica solubility. Values of 13 or higher, however, may result in caustic corrosion or embrittlement, due to excess hydroxide alkalinity.

One proposed system for generation of steam in the oil field is the thermosludge process which was designed to accept produced water directly without the extensive pretreatment required by

conventional once-through steam generators. Table 2-4 presented treatment requirements for these generators. The main requirement would be removal of free and emulsified oil, most likely by a combination of skim tank, induced gas flotation and demulsifier addition. This process has been used in the U.S. and Canada, but has not gained commercial acceptance. Water-side scaling, foaming, and oil fouling problems have been reported, and capital and operating costs normally exceed conventional systems (CH_2M Hill, 1982). As well, problems with corrosion due to poor oxygen control have been reported.

Although conventional utility type steam generators are not currently used in the oil-fields, they have several potential advantages over those boilers currently used. The technology for these sytems is highly reliable, they are capable of producing higher quality steam (thus improving recycle efficiency), and they permit the use of solid fuel. The main disadvantage discouraging their application to date is the high cost of water treatment necessary to meet feedwater requirements. Generally, to operate at the pressures required for oilfield operations, these boilers require demineralized feed-water. Table 2-5 illustrates conventional industrial boiler feedwater requirements with variations in pressure. For these boilers, feedwaters must be essentially free of organic compounds as well.

TABLE 2 - 5

(from Simon, 1975)

GUIDELINES FOR WATER QUALITY IN MODERN INDUSTRIAL WATER TUBE BOILERS FOR RELIABLE CONTINUOUS OPERATION[1]

	Boiler Feedwater			Boiler Water		
Drum Pressure (psig)	Iron (ppm Fe)	Copper (ppm Cu)	Total Hardness (ppm $CaCO_3$)	Silica (ppm SiO_2)	Total Alkalinity** (ppm $CaCO_3$)	Specific Conductance (micromhos/cm)
0-300	0.100	0.050	0.300	150	700*	7000
301-450	0.050	0.025	0.300	90	600*	6000
451-600	0.030	0.020	0.200	40	500*	5000
601-750	0.025	0.020	0.200	30	400*	4000
751-900	0.020	0.015	0.100	20	300*	3000
901-1000	0.020	0.015	0.050	8	200*	2000
1001-1500	0.010	0.010	0.0	2	0***	150
1501-2000	0.010	0.010	0.0	1	0***	100

*Alkalinity not to exceed 10% of specific conductance.

**Minimum level of OH alkalinity in boilers below 1000 psi must be individually specified with regard to silica solubility and other components of internal treatment.

***Zero in these cases refers to free sodium or potassium hydroxide alkalinity. Some small variable amount of total alkalinity will be present and measurable with the assumed congruent control or volatile treatment employed at these high pressure ranges.

2.3 Treatment of Oil/Water/Mineral Emulsions

2.3.1 Existing Technologies

2.3.1.1 Design

Oil can be classified by its tendency to separate from the bulk water phase. Free oil is considered to be those large droplets which are readily separable by gravity, dispersed oil describes smaller droplets which may separate due to coalescence, emulsified oil describes oil droplets which do not coalesce or separate, while dissolved oil is that which is soluble in water (Churchill, 1980). Functionally the first three classifications may be distinguished by size. Free oil particles are those larger than 150 microns in diameter, dispersed particles are from 50 to 150 microns in diameter, and emulsions are made up of droplets less than 50 microns in diameter.

A distinction should also be made between oil/water and water/oil emulsions, terms which are often interchanged. Water/oil emulsions, where oil is the continuous phase, generally are treated by well established conventional means; the major difficulty in their treatment is removing the last traces of water. Oil/water emulsions, especially those produced with heavy oil/bitumen, are often very stable and difficult to treat.

For primary oil recovery the well head emulsion is pumped into a treater or series of treater units. Many different types of treaters and/or chemical additions may be used. The simple unit consists of a heated horizontal baffled tank where the initial three phase gas/oil/water split takes place. Treaters may consist of several stages and may include the addition of demulsifying chemicals

or a light hydrocarbon diluent. The choice of treater type used and chemicals added is made based on feed characteristics and the quality of the oil and liquid phase streams produced.

Often the stable bitumen-rich oil phase emulsions (water-in-oil) which may be produced during the initial primary separation, may contain up to 40% water. It is reportedly difficult to economically remove sufficient water to meet water content specifications of 0.5% in the product oil. The use of hydrocarbon diluent reduces problems associated with water-in-oil emulsions.

The produced water which typically still contains up to 5000 mg/L oil is then directed to treatment for gross oil/water separation. The most common technique for gross oil/water separation in produced water after the treaters at the present time is gravity separation, such as a skim tank or corrugated plate interceptor. Demulsifying chemicals are commonly used. In general these are high molecular weight alkylene oxide polymers, high molecular weight polyesters prepared from ethylene oxide, or other molecules containing large hydrophobic or hydrophilic portions (McCoy et al, 1982). Following skim tanks, the most popular separation technique for oil recovery has been induced gas flotation, using natural gas, with de-emulsifying chemical addition. Often this treatment is then followed by a polishing filter, utilizing diatomaceous earth, cartridge, or sand filtration.

The actual treatment schematic depends on produced water quality and treatment objectives. Current treatment systems include those designed for deep well injection and recycling for steam generation. Re-injection may only require oil removal to prevent

formation plugging, while the more sophisticated recycling systems incorporate a series of unit operations, and may employ combinations of settlers, chemical additions, filters with different media, and softeners. Although several recycling schematics are used, Figure 2-2 prosents what is considered a typical produced water treatment schematic in Alberta.

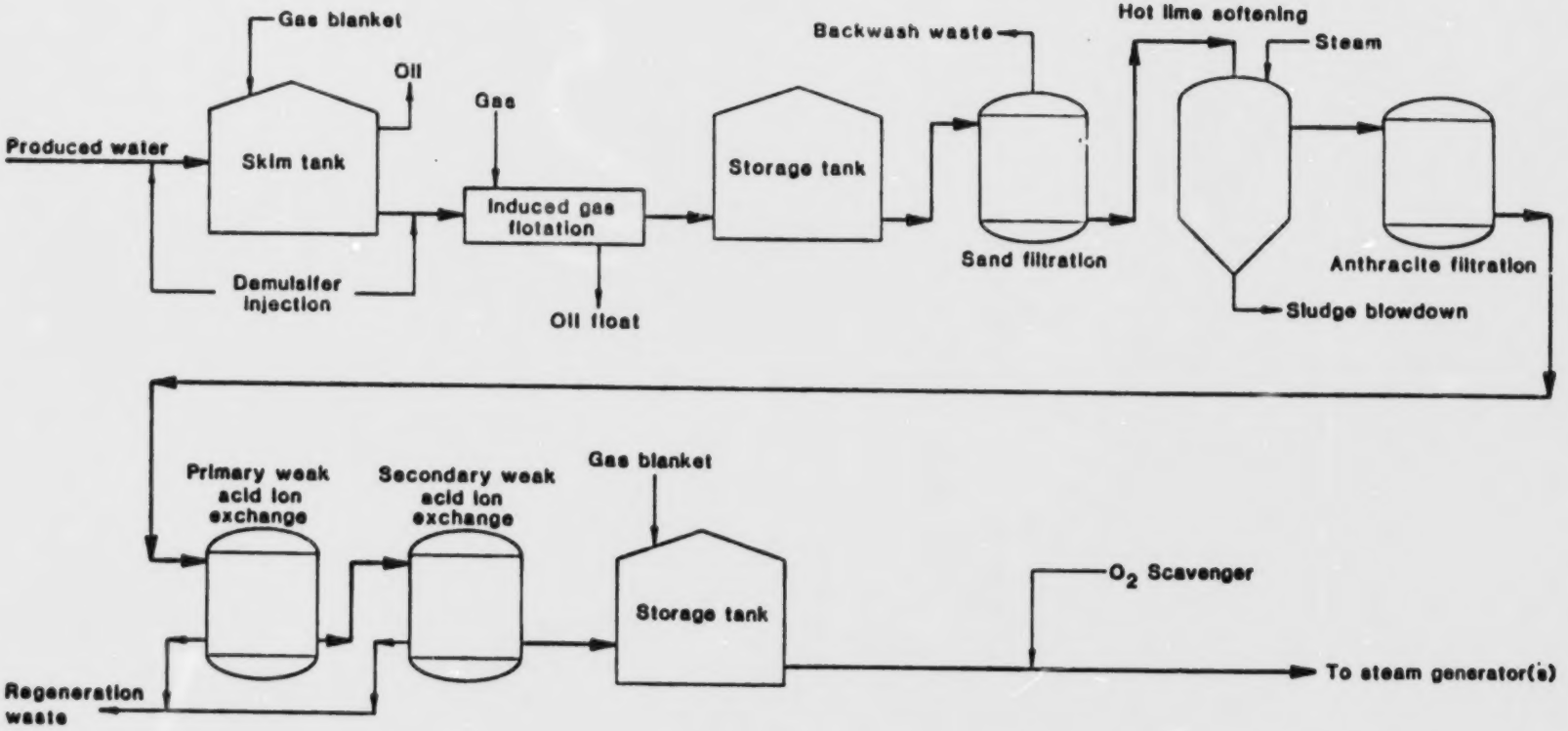
The recovery of emulsified conventional oil from process waters has been researched by many industries, based on payback considerations as well as regulatory requirements which limit effluent concentrations. One such industry is petroleum refining, where environmental regulations strictly limit effluent levels. Typically, free and emulsified oil is treated by dissolved air flotation (DAF) (or similar units) after gravity separation. Luthy et. al. (1978) investigated removal of emulsified oil from refinery wastewaters by the use of various organic coagulants combined with dissolved air flotation. The research found that flocculation with polyelectrolytes prior to DAF may improve operations, but DAF oil removals tended to decrease when suspended solids levels approached 1000 mg/L.

Oil/water separation has also been investigated by the offshore oil industry, and studies have evaluated the use of dissolved air flotation combined with organic coagulants (Snavely and Yarbrough, 1983). Sylvester and Byeseda (1980) studied the process of induced air flotation for oil/water separation in wastewater from all facets of the petroleum industry and found that only oil droplets larger than 2 microns showed significant removal rates by conventional techniques. Dissolved gas flotation has the capability of producing smaller microbubbles than induced gas flotation and hence of producing better

FIGURE 2-2

PROCESS SCHEMATIC FOR TREATMENT OF PRODUCED WATER TO ONCE-THROUGH STEAM GENERATOR FEEDWATER QUALITY

(from CH_2M Hill, 1982)



oil separation. Application of DGF has been limited in produced waters, due to lack of applications research, higher temperatures which limit gas solubility, and potential equipment corrosion problems. Because of the complexity of these particular emulsions, which are stabilized by colloidal clay, asphaltenes, and resinous acids, conventional emulsion breaking techniques such as those used by other industries may not be effective or economical.

2.3.1.2 Economic Evaluation

The costs of the current technologies for oil removal depend on the process flowrate, and specific units and chemicals required to treat the particular produced water stream, thus an economic assessment is difficult. A recent study by CH_2M Hill (1982), however, developed a cost assessment of what was considered to be a typical produced water treatment process, and their results are presented in Table 2-6. The costs were based on a 73 MW capacity boiler requiring a feed of approximately 500,000 USGPD. The costs developed for the Thermosludge process included removal of oil by a skim tank, with demulsifier addition, followed by induced gas flotation. Thus the capital cost for oil removal, as commonly practiced in the oil field, can be estimated to be in the order of $880,000, in 1982 dollars, or approximately 13% of treatment for a conventional system including oil removal. Operating costs for the oil removal system were estimated at $300,000 per year.

TABLE 2 - 6

CAPITAL AND OPERATING COSTS OF CONVENTIONAL ONCE-THROUGH AND THERMOSLUDGE BOILERS ($1000)
(from CH_2M Hill, 1982)

ITEM	CONVENTIONAL ONCE-THROUGH		THERMOSLUDGE	
	GAS-FIRED	CRUDE-FIRED	GAS-FIRED	CRUDE-FIRED
Capital Cost:				
Boiler feedwater treating facilities	$ 6 800	$ 6 800	$ 880	$ 880
Steam generator facilities	4 195	4 195	12 100	12 100
Air compression	-	-	-	-
BFW pumps	750	750	-	-
Fuel facilities	-	120	-	120
Miscellaneous	-	80	-	80
Contingency (20%)	2 690	2 730	2 640	2 680
Total	$14 435	$14 675	$15 620	$15 860
Operating Costs: (Per Year)				
Boiler feedwater treating (including 10% contingency)	$ 985	$ 985	$ 300	$ 300
Steam generation				
Fuel:				
Natural gas	5 695	-	6 435	-
Crude	-	10 415	-	11 765
Coke/Coal	-	-	-	-
Limestone	-	-	-	-
Maintenance	105	105	435	445
Electrical power	110	115	110	115
Operators	245	245	245	245
Waste disposal and misc.	75	75	125	125
Rental fees	-	-	-	-
Contingency (10%)	620	1 095	735	1 270
Total	$ 7 835	$13 030	$ 8 385	$14 265

2.3.1.3 Technical Evaluation

Present oil-field steam generation practices use crude oil or natural gas as fuel. Estimates have indicated that on the average, in oil-fired generators using crude oil, one barrel of crude out of every three barrels produced is burned as fuel (Davis, Young and Lyons, 1981). This illustrates that, in addition to other obvious economic considerations, it is critical to recover as much oil/bitumen as is possible. However, due to the stability of the emulsions associated with oil/bitumen production, concern has been expressed regarding the consistent effectiveness of current technologies for breaking these emulsions.

A study by CH_2M Hill (1981) examined potential unit operations for gross oil and fine oil removal which have either been used or considered for the treatment of produced water from heavy oil fields. A summary of their assessment along with other comments obtained from the literature is presented in Table 2-7.

Conventional gravity separation techniques such as the use of skim tanks provide effective gross oil separation. However, examples can be given illustrating some concerns associated with use of these units in heavy oil/bitumen applications.

Konak and Grisard (1980) state that traditional gravity settling techniques (API separation, skim tanks) etc. are inherently slow and inefficient on bitumen and heavy crude produced waters in which oil density is very close to that of water; furthermore high viscosity and surface tension prevent droplet coalescence even after contact has been made. As a result, performance of both gravity settling devices (skim tanks, API separators, plate settlers) and

TABLE 2 - 7

UNIT OPERATION ASSESSMENT OF CURRENT TECHNOLOGIES

(adapted from CH_2M Hill, 1981)

Unit Operation	Advantages	Disadvantages And Constraints
Gross Oil and Solids Removal		
Above Ground Skim Tank	Proven operation, Simple design Low capital cost, Easily covered Provides some surge volume for oil and emulsions. low energy consumption	Limited and variable effeciency Requires large area Sludge withdrawal problems Potentially labor intensive Susceptible to corrosion
Fine Oil Removal		
Induced Gas (Air) Flotation	Proven technology Considerable experience with gas Removes suspended solids as well as oil Can treat emulsion with chemical treatment Less expensive than DAF, Smaller in size than DAF Lower pumping requirements than for DAF	Relatively high energy requirement Chemical handling and storage facilities req'd. Potential float disposal problems Susceptible to process upsets
Dissolved Gas (Air) Flotation	Proven technology with air Can treat emulsion with chemical treatment Removes suspended solids as well as oil	Susceptible to process upsets Relatively high energy requirement Chemical handling and storate facilities req'd. Little experience with gas other than air Potential float disposal problems Efficiency loss at higher temperature
Granular Media Filtration	Well understood technology Wide range of media to suit application Readily available, Simple design Suspended solids removal as well as oil Can be used on high temperatures	Susceptible to process upsets Periodic media replacement Backwashes must be suitabley treated Prone to mud-balling in oily water service
Precoat Filtration	Proven technology, Relatively compact Flexibility in meeting variable conditions Removes solids in submicron range Removes trace quantities of oil Can be completely automated	Spent filter cake disposal required Relatively high capital cost Relatively high operating cost

coalescing devices (coalescers, media filters) would be lower than expected based on experience with paraffinic oils. Brougham (1978) reports the density of bitumen is lower than that of water at temperatures between 37° and 115°C and higher at temperatures below 37°C. While typical oil-field water treatment temperatures after the treaters are above 37°C, a sinking rather than floating oil layer may result if temperatures decrease.

The two most common techniques for fine oil removal, induced gas/air flotation and dissolved air/gas flotation, can treat these emulsions with potentially costly chemical treatment. Generally effluents from these units still contain about 10-20 mg/L oil, with estimates as low as 5 mg/L under optimum conditions (Behie et al, 1982). This level is usually further reduced by some type of subsequent filtration. Some of the problems expressed in the literature associated with filtration are listed in Table 2-7. In addition the oil trapped in the filters is not always recoverable.

There is a lack of operating information available in the literature on the efficiency of oil-field oil and suspended solids removal systems. Thus any evaluation of the technology used must to a large extent be based on an examination of the nature of the wastewater, properties of the oil to be removed, suitability of the unit processes based on experience in other applications, and general knowledge of wastewater treatment technology, design principles, and practices. Complex phenomena are involved in simultaneous removal of emulsified oil and coarse and fine suspended solids with widely varying particle sizes, surface charge, and relative concentrations in the presence of emulsion stabilizing agents. Present practice has

apparently evolved from adaptation of existing oil removal and boiler feedwater treatment technology and experience in other applications, initally and mistakenly judged to be similar. This is because, as in many other rapidly developing fields, research and understanding of fundmentals has lagged behind applications.

Induced gas/air flotation and dissolved air/gas flotation are generally suitable processes for oil removal with appropriate chemical addition, and are usually reasonably economic and cost-effective processes. However, several limitations have been identified. Sylvester and Byeseda(1980) found that induced gas flotation was unable to significantly remove oil droplets with a droplet size of 2 microns or less. This implies that a fraction of the emulsified oil will not be effectively removed by these units. Oil droplet and gas bubble diameters, liquid residence time, and cationic polyelectrolyte dosage were the most significant variables affecting overall performance. Of these factors, polyelectrolyte dosage is the only one easily changed in an operating system running at design throughput.

The deficiencies of currently utilized unit processes appear to be of several types. Firstly individual unit operations are inherently unable to achieve the necessary levels of efficiency to permit reducing the number of treatment stages. For oil and suspended solids removal a maximum of two process steps, for gross oil and solids removal, and fine oil and solids removal would appear desirable, but current treatment trains utilize more steps at lower individual efficiences. Secondly, some individual processes are only marginally suitable for the service selected, and are inherently

unable to handle surges in inlet concentrations or hydraulic loadings without loss of efficiency. Because of the low rate of separation of heavy oil in gravity devices, hydraulic surges can potentially result in serious losses in efficiency and high outlet oil concentrations.

Experience in other applications has shown that granular media filters, although effective for removal of turbidity, are unable to remove high oil concentrations. In granular media, oil removal is a complex function of direct filtration, coalescence, and adsorption onto filtered solids. While oil removal capacity of media filters is quite limited, it may be enhanced by a variety of techniques, including the use of rougher media such as anthracite and by addition of a coagulant to provide flocculant solids trapped within the filter media onto which oil droplets can adsorb. Nonetheless sudden high concentrations (slugs) of oil tend to break-through filter media into the effluent. This is often followed by mud-balling of the fouled media and associated backwashing problems.

Finally process control technology for individual unit processes is generally relatively primitive, and does not permit automated feed-back or feed-forward control, based on measurement of changes in key process operational parameters, to head off losses in efficiency. This is a general problem in many areas of wastewater treatment, and control is most desirable in those processes in which outlet concentrations respond most strongly to changes in inlet concentration. In coagulation, for example, the state-of-the-art does not permit reliable automated adjustment of coagulant dosage based on resultant tubidity. A similar type of control is desirable but non-existent in induced air flotation units. A recent laboratory study

carried out on removal of oil from produced water by gas flotation (Strickland, 1980) concluded that no correlation between basic system properties and attachment efficiency of gas bubbles to oil-droplets could be found. Furthermore while some important parameters of performance were determined by cell design, others were characteristics of the feed. Therefore the same unit will produce different oil concentrations on different feeds, and effluent from a given cell would change if feed characteristics change. Salinity, oil droplet size, and oil concentration all influenced performance. Because fundamentals are so poorly understood it is premature to discuss better process control in these units. Another recent laboratory study (Behie et al, 1982) concluded that while very high efficiencies were potentially achievable with induced gas flotation, the improper design of only one important element of a unit (e.g. air sparger) can result in very poor performance even if all other elements are well designed. Problems can be expected to be particularly acute whenever feedwater concentrations change severely and rapidly.

2.3.2 Emerging Technologies

Numerous alternative unit processes are being investigated and some have been piloted by the oil industry. API separators, common for the treatment of refinery wastewaters, and corrugated plate interceptors have been investigated for gross oil removal. Although both these techniques may show potential for free oil removal, they are not effective on emulsions.

Chemical coagulation is one alternative process which has received very limited study for treatment of emulsified oil. In particular one potentially applicable technique is to utilize coagulant flocs as oil adsorbents then use DAF to separate the oil-laden flocs from the oily water and subsequently recover oil from the flocs. This technique is widely used at large scale in the primary steel and aluminum industries and automotive industry for treatment of cold rolling and stamping emulsions respectively.

One option under investigation is the use of coalescers, based on adsorption of the oil onto a solid surface. Many types of media have been successfully applied in coalescers and include; granular polymeric resins, specially treated sand, and polyurethane foam. In general the application of coalescers for the treatment of produced water has been limited in the past by a number of factors. Traditional coalescers are designed for treatment of oily wastewaters with negligible suspended solids concentrations operated in an upflow configuration; however, high concentrations of suspended solids cannot be handled by this configuration as the solids will plug the media and cannot be removed by backwashing. Furthermore, very stable emulsions caused by relatively large quantities of surfactants often must be pretreated by the addition of de-emulsifiers. Another factor that has limited the application of coalescers is that many of the traditional coalescing media will not tolerate the higher temperatures of produced waters. As a result it seems likely that applications would be limited to use as secondary or polishing filters. Further development of these technologies will depend upon the development of economical

oil recovery processes and the application of inexpensive or easily regenerated adsorbents.

Extensive research is being conducted in the development of alternative techniques for breaking of bitumen/water emulsions. In an effort to assess alternate processes of emulsified oil separation, Konak and Grisard (1980) examined deoiling of Cold Lake produced water by acidification. Although chemical demusifiers were in satisfactory operation at Cold Lake, the process was examined as a back-up technology directed at situations where the dissolved organic content was a concern and to assist in reducing hydrogen sulfide concentration. They found that acidification with a variety of acids, including sulfuric, hydrochloric, nitric, and acetic, to pH of between 4 and 4.5 was successful in deoiling produced water, as well as in reducing dissolved organic matter and sulfide more effectively than with demulsifiers.

Nagendran and Hrudey (1981) investigated the use of electrolytic flotation techniques in treatment of emulsified oil in Cold Lake produced water. Although the treatment showed promise, costs of required chemical coagulants were prohibitive.

Demulsifiying chemicals have been studied extensively. A process patented by Farnand (1983) found that addition of a combination of formic acid, oxalic acid, and SO_2 was effective in breaking oil/water emulsions typical of in-situ bitumen/heavy oil operations. A variety of organic and inorganic acids, salts, and commercial demulsifiers where tested, of which formic acid was most effective with least side effects. Some adverse effects of using mineral acids have been claimed to be clay attack and associated

flocculation. The reasons for the particular effectiveness of formic acid for this application are not fully understood. McCoy et. al. (1982) patented a process for breaking bituminous emulsions using water soluble demulsifiers consisting of ethylene oxide and propylene oxide polymers (molecular weights greater than about 10,000), at temperatures between 25 and 120°C. Several other patents have been filed in the U.S. using various combinations of polyols, with and without other additives. A Texaco patent (U.S. Patent No. 4,058,453) described a similar process for breaking tar sand emulsions with high molecular weight ethylene oxides and the optional addition of an alkali earth metal.

A review of polar demusifying agents for heavy oil emulsions by Farnand (1981) found aliphatic polar compounds containing oxygen in their functional groups and with a molecular weight of 80 to 200 were most effective. Aliphatic acids, alcohols and ketones were proposed as acceptable additives because they were inexpensive, non-toxic, biodegradable, and readily recoverable.

An investigation of emulsions from the steam injection operation of Norcen Energy Resources, was undertaken by Majid and Farnand (1980). Numerous additives were tested and evaluated, and the authors found that the emulsions were treatable with suitable additives, and water content was reduced from about 70% to below 1%.

One proposed process of breaking oil/water emulsions from in-situ oil recovery involves adding the emulsion to an aqueous coal slurry (Rowat, 1980). The oil attaches to the surface of the coal particle while water is rejected due to the hydrophobic nature of the coal.

A patent for breaking small emulsions of a diameter at least 0.02 microns, was filed by Bitter and Reynhout of Shell International Research (1980). The process investigated a micro-pore ultrafiltration membrane, consisting of hydrophilic and oleophilic zones whose pore size diameter is at least twice the diameter of emulsified droplets, with a recommended maximum pore size of 10 microns. The process functioned not by concentrating the oil in a concentrate stream but by providing surfaces for the coalescence of the emulsified oil to take place. The entire flow is passed through the membrane and is followed by a gravity separation of the two phases.

In recent years, the potential of ultrafiltration membranes for treatment of bitumen/water emulsions has been indicated. Although little published information specific to this application is available, some promising research has been undertaken. Application of ultrafiltration to the treatment of other industrial emulsified oily wastes has been proven to be efficient and economical. A more detailed discussion on this emerging technology will be presented in section 3.0.

2.4 Preparation for Use As Boiler Feedwater

2.4.1 Existing Technologies

2.4.1.1 Design

In addition to removal of oil/bitumen, produced waters must meet all other objectives for boiler feedwater, as discussed in section 2.2.2. Processes for boiler feedwater preparation are used

routinely in many industries, although flow schematics may vary from those used in heavy oil recovery operations.

For hardness removal, the most common technique is ion exchange softening. The type of resin chosen depends on the upstream total dissolved solids level. The Esso Resources Cold Lake project is one large - scale system which employs hot lime softening for simultaneous reduction of both hardness and silica.

Getty Oil Company, in the Kern River Field near Bakersfield, California, operates one of the largest produced water recycling systems for production of boiler feedwater and treats approximately 80,000 m^3/day of produced water (Carrell, 1979). The treatment successfully employed consists of chemical treatment, induced gas flotation (depurator unit), sedimentation, nitrogen gas flotation, pressure cake filtration (diatomaceous earth), and cation exchange softening. Figures 2-3 and 2-4 illustrate the water quality treatment sequence, and unit removal efficiencies. The operators claimed that oil concentration was one of the most critical factors in plant operations due to the adverse effect on filter operations. Removal of 90% of the oil is accomplished by the initial IGF (depurator) in a single step while removal of the remaining 10% requires a series of steps. Removal of suspended solids requires a series of steps. Removal of hardness is achieved by the simple step of cation exchange softening. The multiple steps involved for removal of oil and suspended solids indicate an undesirable lack of efficiency in each stage. The use of diatomaceous earth pressure filtration is also generally indicative of the presence of colloidal, sticky, gelatinous or other difficult to remove materials in the water to be

FIGURE 2 - 3

WATER TREATMENT PROCESS AT KERN RIVER
(from Carrell, 1979)

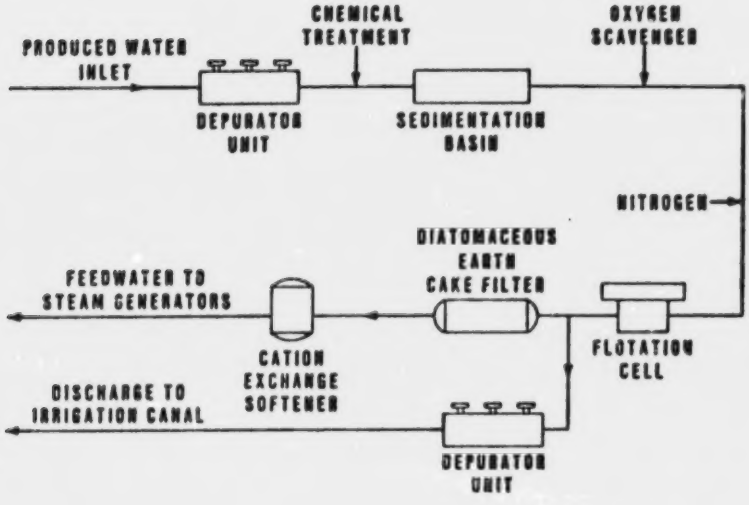
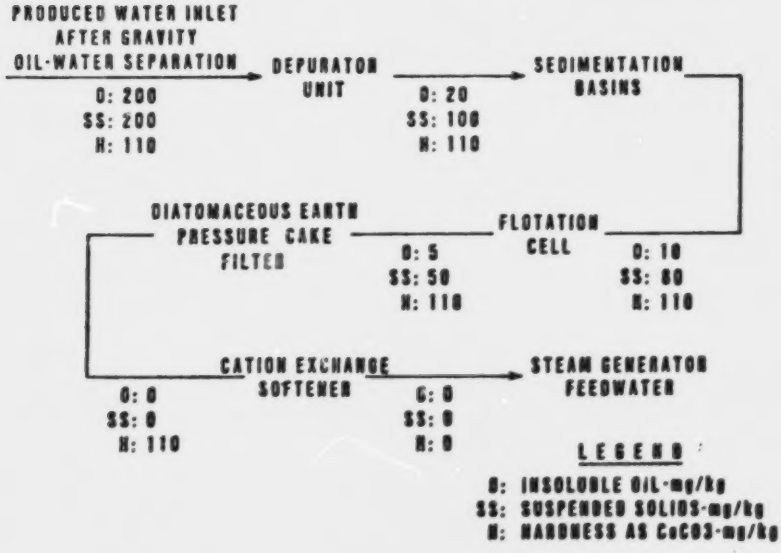


FIGURE 2 - 4

UNIT REMOVAL EFFICIENCIES AT KERN RIVER
(from Carrell, 1979)



treated, and results in loss of the oil removed with the discarded diatomaceous earth.

The process developed for water recycling in Cold Lake is shown schematically in Figure 2-5. The key elements of this process are deoiling (by induced gas flotation), softening (by hot lime softeners), and deionization by ion exchange. As shown in this Figure, make-up water is combined with produced water prior to entering the treatment process.

Whalley and Wilson (1979) discuss the various other treatment process schematics which were evaluated for the Cold Lake project before selection of the system described previously. These are presented in Figure 2-6, with technology assessment shown in Table 2-8. Three potential schemes investigated utilizing drum-type utility boilers. In one scheme (Figure 2-6c) desalination (by evaporation or membrane techniques) of produced water was to be followed by demineralization of combined pre-treated produced water and make-up water. The other two schemes using utility boilers handled the treatment of produced water in a relatively conventional manner, and terminated with a softening step. Introduction of make-up water prior to softening helps in reducing hardness leakage.

A recently expanded thermal pilot project operated by Suncor Inc. near Bonneyville, Alberta is expected to require 3,700 m^3/day of steam generator feedwater (Kloepfer and Kus, 1983). However, the fact that the produced water contained TDS levels up to 20,000 mg/L (versus approximately 6,000 in Cold Lake) resulted in a decision to recycle only up to 50% of the produced water, and supplement it with local municipal wastewater. The processes selected for treatment of this

FIGURE 2 - 5

PROCESS SCHEMATIC FOR RECYCLE OF PRODUCED WATER FROM CYCLIC STEAM STIMULATION BITUMEN RECOVERY AT COLD LAKE (Imperial Oil, 1978)

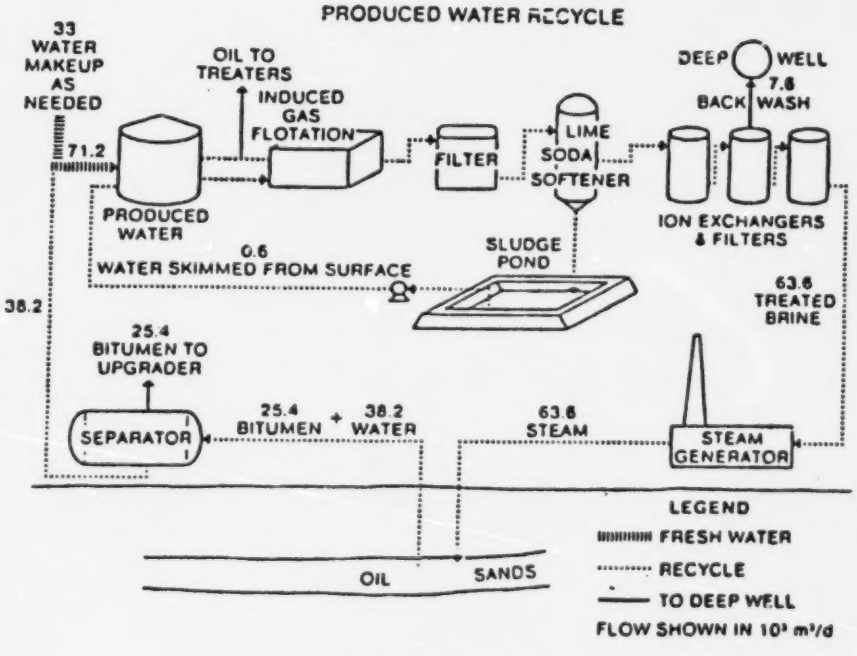
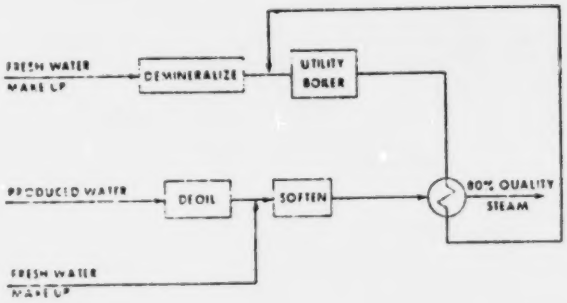


FIGURE 2 - 6

POTENTIAL WATER RE-USE SCHEMES
(from Whalley & Wilson, 1979)

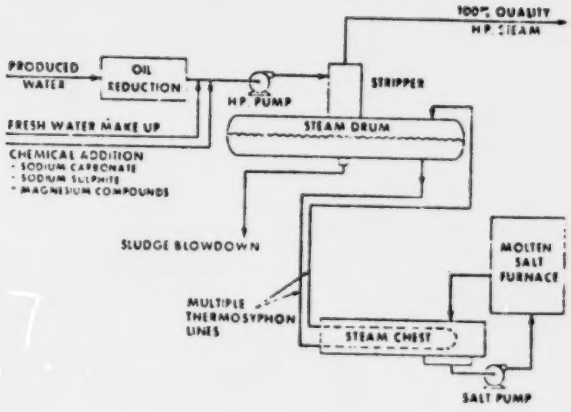
a)

REBOILER REUSE SCHEME



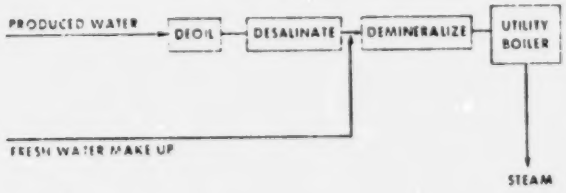
b)

THERMOSLUDGE GENERATORS



c)

UTILITY BOILER REUSE SCHEME



d)

SUPERHEAT/DESUPERHEAT REUSE SCHEME

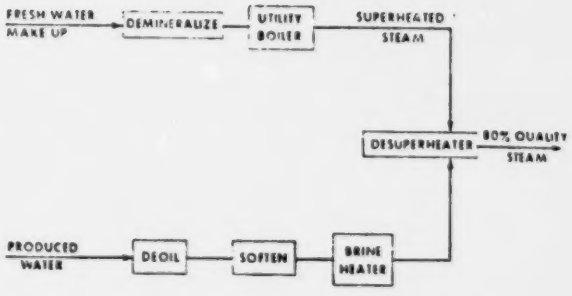


TABLE 2 - 8

ASSESSMENT OF POTENTIAL WATER REUSE SCHEMES EVALUATED FOR COLD LAKE

(Whalley & Wilson, 1979)

Potential Water Reuse Schemes.

Scheme	Water Treatment	Steam Generation
1.	Deoil, Desalinate, Demineralize	Utility-Like Boilers–100% Make Up
2.	Deoil, Soften	Utility Boilers–Reboilers
3.	Deoil, Soften	Utility Boilers–Superheat/Desuperheat
4.	Oil Reduction	Thermosludge Generators
5.	Deoil, Soften, Silica Reduction	Conventional Steam Generators

Relative Merits of Reuse Schemes.

Attribute	Utility Boilers	Reboilers	Superheat /Desuperheat	Thermosludge	Conventional Steam Gen.
Flexibility	Limited	High	High	High	High
Cost	Very High	High	High*	Moderate	Low
Technical Certainty	Moderate	High	Moderate	High	High
Ability to Fire Coal	High	High	High	Low	Low

*High if coal-fired, only moderate if gas-fired.

stream include chlorine disinfection, lime/soda softening, filtration, and ion exchange. Operating data has not been reported in the open literature.

2.4.1.2 Economic Evaluation

For later comparison with UF/RO treatment, total capital cost from Table 2-6 of a complete treatment system based on a flow of approximately 500,000 USGPD is estimated to be $6,800,000 ($CH_2M$ Hill, 1982). Operating costs were estimated at $985,000. In section 2.3.1.2, the capital and operating costs of typical conventional systems for oil removal were estimated at $880,000 and $330,000 per year, respectively. Substracting these from the cost of total treatment yields a rough estimate of the cost of processes for achieving boiler feedwater quality after oil removal. Therefore the capital and operating costs for a process employing sand filtration, hot lime softening, anthracite filtration, and primary and secondary ion exchange are estimated at approximately $6 million and $700,000 respectively.

2.4.1.3 Technical Evaluation

Although information on the design of typical unit processes can be obtained, there is little information published regarding the effectiveness or efficiency of water recycling systems presently in use in the oil-field. Problems may be encountered in the following treatment stages when used:

i) Lime softening (in particular when there is a high silica content) and lime sludge disposal.

ii) Ion exchange fouling due to organic content.

iii) Boiler scaling

iv) Corrosion of piping and other equipment.

Very high demands are placed upon the technology for recycling in-situ water and, therefore, the likelihood of problems relating to the above areas is also high, especially during the initial start-up phases. Although the Cold Lake project has proven the technical feasability of recycling produced water, concerns have been expressed in the industry regarding cost, reliability, and process control (Card and Kus, 1983).

The main technologies in current use for the recycling of produced water from heavy oil/in-situ bitumen operations have been adapted from classical boiler feedwater treatment principles as used in other industries. The main adjustments made are a consequence of the higher levels of TDS (brine), dissolved gases, and silica encountered. The major strength of existing systems is that not withstanding some problems systems are operational and functional for the recovery of oil and generation of boiler feedwater. Current technologies have permitted substantial amounts of produced water to be treated and recycled for use in once-through steam generators.

The limited information available on their operating efficiencies has indicated that these systems are generally satisfactory with respect to treatment objectives, however many systems are complex and expensive to operate. They often require a large number and variety of specialty chemicals, a high level of process monitoring, skilled service by water treatment chemical

suppliers, and special maintenance procedures to keep equipment operational. Additionally large amounts of commodity chemicals are used which may generate significant quantities of sludge or liquid wastes requiring subsequent disposal. These include lime for softening and brine for ion exchange regeneration. A frequently occurring but not widely publicized problem with the type of treatment train commonly used is that water-soluble polar organics are prone to fouling weak acid ion-exchange resins, leading to loss of exchange capacity.

Greater simplicity is desirable in oil-field treatment systems. The limited recycle practised to-date is a result of the economical and technological limitations of current systems, and suggests that more cost-effective processes are needed.

2.4.2 Emerging Technologies

The technologies currently utilized are various combinations of well established conventional processes similar to those utilized by other industries. One technology offering considerable potential for this application is the use of reverse osmosis for boiler feedwater preparation. Section 3.0 discusses membrane processes in general, and related industrial applications of membrane technology which serve to illustrate the potential efficiency and cost-effectiveness of membrane processes for treatment of oil-field produced waters.

3.0 APPLICATION OF MEMBRANE TECHNOLOGIES FOR TREATMENT OF PRODUCED WATER

3.1 Background

In recent years, both research and applications of membrane technologies for the treatment of various waters and industrial wastewaters have increased. With improvements in operating efficiences, widespread commercial acceptance of large scale systems has also occurred.

The commonly used pressure driven membrane process are ultrafiltration (UF) and reverse osmosis (RO). Ultrafiltration is a low pressure membrane process, suitable for separation of particulate and colloidal material and large dissolved organic molecules. Reverse osmosis is a high pressure membrane process utilized primarily for separation of ions and smaller dissolved organic molecules. In both cases, separation is accomplished by selective passage of components through a membrane with specific characteristics. A relatively pure "permeate" passes through the membrane and is collected, whereas rejected materials are concentrated in the "concentrate" or "retentate".

Table 3-1 summarizes and compares the characteristics of these two processes, and illustrates membrane separation ranges and process effectiveness compared to conventional treatment.

The treatment of produced water for use in once through steam generators requires removal of essentially all oil, hardness, and suspended solids, and often reduction in silica and dissolved solids. The use of ultrafiltration for removal of emulsified oil from industrial waste streams has been well documented, and large scale

TABLE 3 - 1

SUITABILITY OF PROCESS

Contaminant / Process	Particulate Matter >10 u	Particulate Matter >2 u	Particulate Matter >.2 u	Colloids ≥100 A	Dissolved Inorganics (ions)	Dissolved Organics >10,000 MW	Dissolved Organics >100 MW	Membrane Pore Size A^0	Typical Applied Pressure psi	Typical Applied Pressure kpa
Ultrafiltration	Excellent	Excellent	Excellent	Excellent		Excellent	Fair	50 - 500	20-100	138-690
Reverse Osmosis		Excellent	Excellent	Excellent	Good	Excellent	Good	5 - 50	200-800	1380-5520
Inert Media Filtration	Excellent	Good								
Adsorption	Excellent	Good				Excellent	Excellent			
Microfiltration	Excellent	Excellent	Good							
Deionization					Excellent					

reverse osmosis units are now commonplace for treatment of seawater, boiler feedwater, and metal finishing waters. The technical and economical advantages of these related applications illustrate the potential for UF/RO application in the treatment of oilfield produced waters for steam generation.

3.2 Treatment of Oil/Water/Mineral Emulsions by Ultrafiltration

3.2.1 Process Description

Ultrafiltration is basically a low pressure membrane filtration process on the molecular level by which solvent and solute molecules are separated by shape and size with some degree of influence from ionic strength and the pH of the solution. Ultrafiltration membranes typically have a pore size of 50 to 500 angstroms.

Figure 3-1 shows the process of passing a feed solution under turbulent conditions, under pressure across the UF membrane surface. In this process the small molecules pass through the pores of the membrane and as the feed solution passes over the membrane surface it becomes more and more concentrated with large molecules.

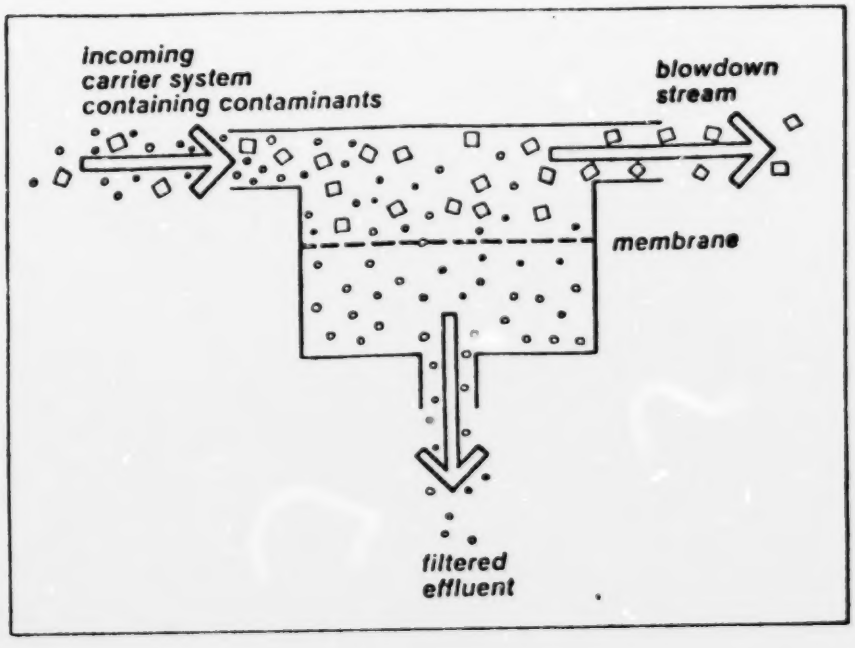
Permeate rate is a function of applied pressure, temperature, turbulent pumping flow, steric effects, and the degree of concentration polarization. Operating pressures typically range from 20-100 psig (138 - 690 kPa). Flux, a term used to describe membrane performance, is defined as the rate of permeate flow per unit area of membrane per unit time.

Ultrafiltration can be used to selectively concentrate valuable components from wastestreams, and has been commercially

FIGURE 3-1

MEMBRANE ULTRAFILTRATION PROCESS

Wastewater is pumped under pressure to the semi-permeable membrane which permits passage of small molecules but retains the large ones.



accepted as a treatment for oil/water emulsions. The open literature contains information on systems upwards of 100,000 gpd in size which have been successfully employed for this application. Depending on membrane type and configuration, systems can be designed to totally remove flocculants or suspended solids, as well as colloids and turbidity.

The stability of oil/water emulsions is enhanced by the prescence of surfactants, which lower the interfacial tension and reduce oil coalescence. Surfactants may be naturally occurring compounds, compounds added to promote emulsion stability at other stages of the process or by-products of industrial processes. The surfactant molecule generally consists of a long chain compound with an oil soluble, non-polar "head" and a large water soluble, polar "tail".

Ultrafiltration separates compounds on the molecular scale, and in industrial oily water applications, a varying proportion of the smaller surfactant molecules may pass through the membrane, while the larger oil particles would not. The loss of the emulsion stabilizing agent with the water in the permeate could therefore cause the oil/water emulsion to break down and release free oil. Depending on the membrane affinity for oil this may result in formation of an oily layer on the membrane surface, accompanied by a gradual decrease in permeate rate with time. However, the rate can often be restored to its original value with cleaning at appropriate intervals. It is also possible that the oil droplets remaining during concentration of the emulsion may coalesce due to the increasing oil concentration and not adhere to the membrane surface. Many applications have achieved up to

90% volume reduction, thereby concentrating the oil by a factor of 10. The concentrate with accumulated free oil can be removed and often phase separation actually occurs. Three layers containing recoverable oil, oil/water, and sludge may be separate.

Emulsions from in-situ steam stimulation operations can be highly stable; this stability is thought to be associated with the presence of colloidal asphaltenes and clays, as well as various petroleum acids. Colloidal compounds do not pass through ultrafiltration membranes, and passage of petroleum acids, such as carboxylic acids which are relatively small in molecular weight, is dependent on their affinity to the colloidal suspensions present. However, previous ultrafiltration research on produced water emulsions (Farnand and Poirier, 1983) has suggested these emulsions break at the membrane surface thus implying destabilization may occur due to surfactant or emusifier loss into the permeate. The study indicated the potential for ultrafiltration to break these emulsions, but found that effectiveness is dependent upon the membrane material used.

3.2.2.1 Membrane Materials

To prevent membrane pore clogging by oil, and to allow water to pass through the membrane, hydrophilic and oleophobic ultrafiltration membranes are usually selected for treatment of oily wastes.

There are various ultrafiltration membrane materials commercially available and under development for treatment of oil/water emulsions. Table 3-2 lists the commercially available ultrafiltration membranes, and includes pH and temperature

TABLE 3-2

COMMERCIAL ULTRAFILTRATION MEMBRANES

Membrane Material	Configuration	MW Cut Off	Permeate Rate ($L/m^2/d$)	Pressure (kPa)	pH Range	Temp. (°C)
Cellulose acetate	Spiral	15000	6000	360	3-7.5	50
	Tubular	1000-100000	400-10000	310	2-8	35-50
	Flat	1000-100000	400-10000	310	208	35-50
Co-Polyacrylonitrile/ Methallyl Sulfonate	Flat	20000	7000	206	1-10	40
Modacryl Polymers	Capillary	50000-80000	12000-15000	103	1.5-13	60
Polyacrylonitrile	Tubular	10000	7000	310	4-10	60
Polybenzimidazolone	Tubular	NA	NA	NA	1-12	60
Polyamide	Capillary	2000-50000	100-6000	155	2-12	80
	Tubular	8000-200000	3000-9000	310	2-8	40
Polyolefin	Spiral/Tubular	20000-100000	NA	NA	2-10	40
Polysulfone	Flat	1000-2000	4000-12000	360	1-13	90
	Spiral	1000-80000	2000-4000	516	2-14	50
	Capillary	2000-50000	1000-14000	103	1.5-13	75
	Tubular	5000-50000	8000	310	1-13	40-95
Polyvinylidene FLuoride	Spiral	10000-20000	7500	360	2-12	90
Sulfonated Polysulfone	Flat	8000-20000	1000-15000	310	2-12	80
ZrO_2	Tubular	20000	NA	NA	1-14	>93
Non-cellulosic Hydrophilic Polymeric	Tubular	10000-20000	8150-16000	710	1-14	40
	Flat	5000	5000	890	1-14	100

(adapted from Purch and Welch, 1982)

limitations, and approximate permeate rates based on pure water fluxes for each membrane type.

There are basically three types of commercially available ultrafiltration membranes; cellulose acetate derivatives, polysulphones, and a limited class of other non-cellulosic polymeric membranes. In addition to the commercially available membranes, researchers are continually improving upon and developing new membrane materials. However data is generally not available on many recently developed membranes due to their proprietory nature.

The literature has shown that many companies have demonstrated the efficient and economic concentration and recovery of oil (mineral and vegetable) from oil/water emulsions utilizing ultrafiltration systems. ZENON Environmental Inc. and others, have industrial systems in the automotive industry treating drawing, stamping, and machinery oil emulsions for one or more of the following purposes:

i) To reduce emulsion volume,

ii) To reclaim oil for reuse, or

iii) To produce a permeate suitable for disposal or reuse.

Typically, these systems can concentrate oily waste streams to 80-90% volume reduction up to a 30-40% oil content. Ultrafiltration is also very effective for removal of suspended solids.

To meet one or more of the objectives listed above, the membrane should preferably be hydrophilic. Commercially available hydrophilic membranes include cellulose acetate (CA), polyvinylene

difluoride (PVDF), sulphonated polysulphone (SPS), and thin-film composite (TFC) formulations of these types of membranes. Ultrafiltration membranes such as polysulphone and polyimide, due to their oleophilic nature, can be fouled by oil and hence are usually not thought to be suitable for processing of oil-in-water emulsions. However, the chemical properties of the feed water in combination with chemical composition of the specific membrane may result in surface interactions which cause a decrease the expected fouling rate. Thus laboratory tests are necessary to determine which actual membrane materials are suitable for a particular application.

Reverse Osmosis membranes due to their smaller pore size and pressures used are susceptable to fouling by oil laden feedwaters. No published literature could be found for treatment of oily waste water by reverse osmosis. In addition, all membrane suppliers contacted except for one indicated that all oil must be removed before employing their RO membranes. One manufacture has indicated that a newly developed sulphonated polysulphone reverse osmosis, hollow fibre membrane might be capable of concentrating oil/water solutions.

In addition to membrane characteristics, operating conditions will affect membrane selection. Ultrafiltration membranes are affected by a number of factors which limit the conditions under which they can be operated. These factors include:

i) pH

ii) temperature

iii) resistance to bacteria

iv) resistance to chlorine

v) resistance to solvents

Table 3-3 presents these limitations for five membranes that are viable for oil/water separation.

Generally the pH and temperature limitations for SPS, PVDF, and TFC membranes are due to the deterioration of the membrane housing material. Cellulose acetate membranes may also be degraded by bacteria, and dissolved by organic solvents. Cellulose (CE) membranes are a new class not yet commerically available, however, they offer a greater working pH range and improved organic rejection than cellulose acetate.

Produced water is generally brought to the surface at temperatures above 65°C (150°F). Depending on actual temperatures in the field treatment system, this may require cooling if the cellulose acetate or TFC membranes are utilized. In the case of other membranes, care must be taken to exclude all heat sensitive materials from the membrane module. Current commercial membrane modules include such materials, and therefore, as shown in Table 3-3, emulsion fed to these modules would also require some cooling. The pH of the water is generally slighly alkaline, and well within the acceptable range of the ultrafiltration membranes listed.

3.2.1.2 Configurations

In addition to membrane type, there are several configurations of membranes available. Configurations are selected according to availability, feedwater quality, pretreatment requirements associated with each configuration, and economical considerations. The most common membrane configurations are tubular,

TABLE 3-3

TYPICAL OPERATING LIMITATIONS OF SOME HYDROPHILIC ULTRAFILTRATION MEMBRANES

	CA	PVDF	SPS	TFC	CE	PS	CHP
pH	4-7	2-12	2-12	2-10	4-12	2-12	2-12
Maximum Temp. (°C)	35	60	60	35	35	60	60
(°F)	95	140	140	95	95	140	140
Bacterial Resistance	no	yes	yes	yes	no	yes	yes
Chlorine Resistance	yes	yes	yes	no	yes	yes	yes
Solvent Resistance	poor	good	good	fair	poor	good	good

spiral, and capillary (hollow fine fiber). These are illustrated in Figure 3-2.

In the tubular configuration, the membrane is cast on the inside of a 1/2 to 1 inch diameter porous support tube. The water to be treated flows through the center of the tube, and the permeate passes through the membrane and support tube into a collection vessel. These configurations have a very wide range of operating pressures, and good resistance to plugging by suspended solids due to the high flow velocity. The permeate production per unit volume is however very poor compared to the spiral wound or capillary units. Thus they are not cost competitive at low suspended solids levels, but can be used on streams with large amounts of suspended solids without the pretreatment required for spiral or capillary units.

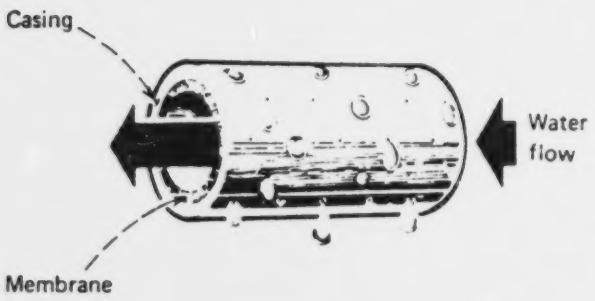
The spiral wound or scroll type membrane has a configuration which provides a high membrane surface area per unit volume ratio. The manufacturing technique involves wrapping a spiral sandwich of two sheets of membrane epoxy sealed along their common edge, and separated by a porous synthetic backing material which forms a channel through which the permeate flows. The permeate travels spirally into a central perforated permeate collector tube running longitudinally up the centre of the module. A polypropylene turbulence promoter acts as a spacer between the spiral roll of the membrane module.

In capillary, or hollow fine fiber configurations, the membranes are spun into hollow fibers which are very fine (100 to 200 micron in diameter) with walls about 25 micron thick. Cylinders with such low diameter do not need a supporting structure to withstand high pressures. Bundles of these long fibers are arranged in a U-shape,

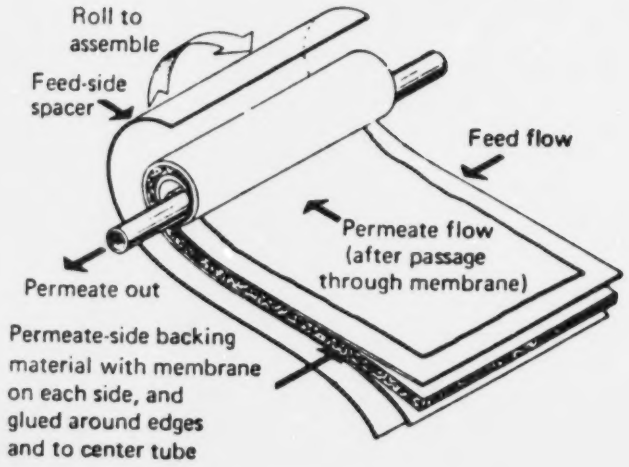
FIGURE 3 - 2

MEMBRANE CONFIGURATIONS

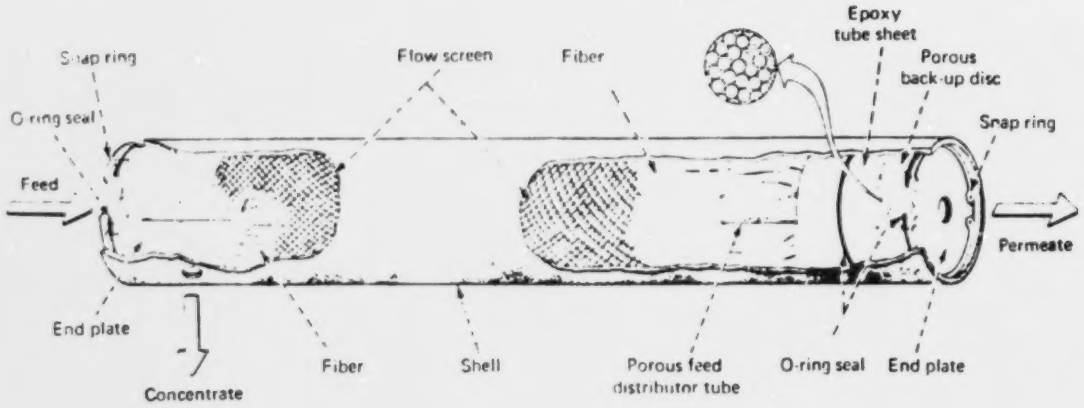
REPRESENTATION OF A TUBULAR MEMBRANE



FABRICATION OF A SPIRAL-WOUND MODULE


Roll to assemble
Feed-side spacer
Feed flow
Permeate flow (after passage through membrane)
Permeate out
Permeate-side backing material with membrane on each side, and glued around edges and to center tube

CAPILLARY(Hollow Fine Fiber) PERMEATOR



and the open ends are "potted" in plastic. This bundle is arranged in a cylinder vessel as shown in Figure 3-2. The feed solution is introduced into the middle of the fibre bundle through a porous tube at one end of the cylinder, and the concentrated product leaves from an effluent tube at the same end. The permeate passes through each fiber to the "potted" end where it is collected. Table 3-4 summarizes relative advantages and disadvantages, along with general pretreatment requirements for each configuration.

Usually configurations are selected based mainly on economical considerations, and spiral configurations, due to the large membrane surface areas, are often preferred for large scale systems. However, the configuration selected does determine pretreatment requirements. All configurations require removal of free oil and larger particulate to some extent. Tubular configurations have the least stringent pretreatment requirements and only require removal of particulate matter larger than 50 microns.

Spiral configurations have a high membrane surface area, and are often preferred for larger-scale applications. However, they generally require removal of particles larger than 5 micron in size and are more dependant on pH, since chemical glues and adhensives are used in the system housing which may be affected by pH, while tubular systmes use mechanical sealing components such as O'rings.

Hollow-fibers have similar limitations as spiral, although have not yet been widely applied in ultrafiltration.

TABLE 3-4

COMPARISON OF MEMBRANE CONFIGURATIONS

Configuration	Advantages	Disadvantages	Status	Pretreatment
Tubular (conventional)	Easily cleaned mechanically or chemically; very tolerant to suspended solids. Much operating experience Individual tubes replaceable	High holdup per unit membrane area Relatively expensive Requires moderately large floor space per sq.ft. although tube modules can be placed separately in and around existing equipment in special cases	Commercial	P, 50
Spiral-wound	Low in cost Compact; low floor space per sq.ft. Low hold up per unit membrane area Much operating experience	Easily plugged Cleaning options are limited	Commercial	P, 5
Hollow-fiber(shell-side feed)	Very low in cost Very compact Low holdup	Plugs easily Very hard to clean	Commercial	P, 5
Hollow-fiber (feed inside fibers)	Very low in cost Very compact Low holdup May be amenable to cleaning	Just now on market-meager operating experience	Fiber modules new on market	P, 5

P = pH Adjustment
5 = 5 micron particle size prefiltration to prevent clogging of the membrane channel of feed flow.
50 = 50 mesh filter to remove particles which would damage pumps.

3.2.2 Current Applications and Economic Evaluation

There is a wide range of applications in industry where ultrafiltration has been proven and is being proven to be a viable alternative for pollution control and product recovery (Lopez and Johnson, 1977; Christensen and Plauman, 1981; Koehler, 1983).

Ultrafiltration has been utilized in treatment of emulsified oily wastes from machining operations, automotive plants, and rolling mill coolants, for either the recovery of oil or production of water suitable for reuse. Due to the general lack of research on ultrafiltration processes specific to oilfield applications, it is necessary to examine efficiency and economics of well-documented applications in other related industries. Typically industrial oil/water emulsions exist at a concentration of 0.5-10% oil in the feed and UF can remove 90-95% of the water in the emulsion up to about 30-40% oil (Dhawan, 1978).

Both cellulosic and non-cellulosic membranes have been successfully employed in industrial applications, depending on feedwater characteristics and treatment requirements. Cellulose acetate membranes have been sucessfully employed in some cases, such as for treatment of cutting oil from the metal working industry (Kutowy et al, 1981), although their susceptibility to hydrolysis at high and low pH has been a limiting factor.

Early research by Goldsmith, et al, (1974) studied the treatment of soluble oil waste from an electric company, which contained 1 to 3 per cent oil, of which 30% was emulsified machine coolants. They used one inch tubular polymeric membranes, and achieved a concentrate oil level of 40 percent. Fouling was not

encountered in this study, and this was attributed to the presence of detergent emulsifiers which prevented an oil build-up on the membrane.

The efficiency of the treatment of stable oil emulsions from the metal working industry by ultrafiltration was reported by Dick (1981). The use of non-cellulosic hollow fine fiber ultrafiltration was found to economically remove 98% of oil with 90% reduction in volume. The oil in the UF concentrate was suitable for further treatment to recover the oil.

A survey of current tubular ultrafiltration systems in use for oily wastewater treatment in various industries (Wahl et al, 1979) found plants as large as 100,000 gpd were successfully and economically operating, and the resulting oil recovery in some cases resulted in breakeven, or even profitable operations, as shown in Table 3-5.

In addition to the well documented efficiency of UF, combinations of UF with subsequent Reverse Osmosis RO application on UF permeate have been used on oily wastewaters for oil recovery, and to produce a water quality suitable for industrial reuse. Mixed industrial wastes containing process wastes such as cutting oils as well as rinse tank waters, cooling tower bleeds, and miscellaneous other wastes, have been treated by UF/RO combinations to provide water quality suitable for direct recycle (Lopez and Johnston, 1977). Reverse Osmosis will be discussed in greater detail in section 3.3.

A combination of UF/RO was used for treatment of oily waste streams in the aluminum industry (Sonksen, 1978). Alcoa investigated and compared the operation and economics of chemical, evaporation, UF, and UF/RO treatment of their wastes. Pilot plant studies concluded

TABLE 3 - 5

SURVEY RESULTS - OILY WASTEWATER TREATMENT SYSTEM ANNUAL COST SUMMARY

(from Wahl et al, 1979)

System	Date of System Start-Up (mo/yr)	Design Flow Rate (gpd)	Actual Daily Flow (gpd)	Direct Labor ($)	Power ($)	Membrane Replacement ($)	Cleaning Chemicals ($)	Concentrate Disposal (Oil Recovery Credit) ($)	Total Cost (Ex. Oil Credit) ($)	Cost Per Gallon (¢)	Total Cost with Oil Recovery Credit (Savings) ($)
1	5/76	18,000	20,000	20,000	6,893	27,653	17,386	(150,000)	71,932	1.4	(78,068)
2	7/77	1,000	800	8,000	895	1,298	653	4,400	15,246	7.6	–
3	12/74	2,500	4,300	3,125	2,954	1,540	6,224	(91,000)	13,843	1.3	(77,157)
4	2/78	1,000	1,100	6,250	1,253	3,060	840	(325)	11,403	4.1	11,078
5	9/75	1,000	500	6,667	895	325	2,000	0	9,887	7.9	
6	7/75	2,500	4,000	5,500	985	0	2,425	0	8,910	0.9	
7	9/75	10,000	6,000	2,857	2,686	139	2,415	(8,550)	8,097	0.5	(453)
8	9/77	3,000	2,000	125	985	0	–	–	–	–	
9	11/75	5,000	5,000	3,000	2,954	2,720	5,510	–	–	–	
10	11/75	8,000	4,000	2,917	2,686	0	277	1,400	7,280	0.7	
11	3/77	4,000	10,000	5,625	2,954	-0	1,750	(9,375)	10,329	0.4	954
12	9/75	20,000	40,000	7,000	6,983	3,338	100	(64,000)	17,421	0.2	(46,579)
13	11/74	4,000	4,000	8,750	2,328	1,322	1,081	(68,640)	13,481	1.3	(55,159)
14	5/76	3,000	3,000	9,286	1,432	1,190	648	3,840	16,396	2.2	
15	6/77	100,000	100,000	20,000	24,170	3,326	17,051	(79,688)	64,547	0.3	(15,141)
16	3/75	1,728	3,000	3,611	985	1,265	200	0	6,061	0.8	
17	12/74	500	500	1,548	985	1,078	48	2,160	5,819	4.7	
18	2/76	15,000	20,000	11,000	5,640	6,277	5,533	(1,700)	28,450	0.6	26,750
19	9/75	980	300	250	895	325	48	30	1,548	2.1	
20	3/75	500	1,000	5,833	985	428	333	–	7,579	3.0	
21	11/74	500	300	3,125	895	2,116	250	–		–	

that UF/RO would provide a superior and reusable product than the chemical treatment system currently employed. Estimated treatment costs (1978 dollars) for a 100,000 gpd plant are presented in Table 3-6. The figures show a slightly lower capital investment for the membrane processes. After one year's operation on full scale, actual operating costs were $0.76/1,000 gal lower for chemical treatment, but this did not include cost of sludge disposal or possible post treatment of oil to meet regulatory effluent guidelines. Problems were encountered with membrane fouling and associated cleaning requirements, but operators still were most satisfied with the combined UF/RO facility based on product quality, lower sludge generation, and lower dependence on operator judgement.

Ultrafiltration has also been shown to be efficient and economical for pretreatment of seawater prior to desalination by reverse osmosis (Hayward and Choate, 1982). The ultrafiltration process was used to retain suspended, emulsified, and colloidal solids, as well as dissolved macromolecules, and produce a permeate which resulted in stable RO productivity and little maintenance or operator attention. The purpose was to prevent fouling, and thereby increase membrane life. After 9,600 hours of operation the RO permeate had not yet required cleaning or regeneration. This pretreatment is now thought be technically excellent and economically competetive with conventional pretreatment, thus illustrating the potential of UF not only for oil removal but also as a pretreatment to RO on waters with high levels of suspended solids or dissolved macromolecules.

TABLE 3 - 6

a) **ESTIMATED COST ANALYSES AT ALCOA PENNSYLVANIA**

(Sonksen et al, 1978)

System	Capital Cost	Total Unit Operating Cost ($/1000 gal)	Net Unit Operating Cost ($/1000 gal)
Chemical	$1,730,000	$11.33	$5.36
Evaporation	2,650,000	8.75	2.90
UF	1,450,000	7.73	1.77
UF/RO	1,550,000	8.81	1.12

b) **OPERATING COST COMPARISONS AT ALCOA**

	Chemical	Ultrafiltration	Ultrafiltration and Reverse Osmosis
Depreciation	$2.58/1,000 gal	$2.44/1,000 gal	$2.69/1,000 gal
Power	0.12	0.47	0.62
Steam	0.10	0.19	0.19
Labor	1.73	2.00	2.00
Chemicals	2.00	1.48[a]	1.48[a]
R & M	1.54	0.92	0.92
Membrane replacement	--	1.61[b]	2.30[b]
Total unit operating cost	$8.07/1,000 gal	$9.11/1,000 gal	$10.20/1,000 gal
Credit for water recovery	--	$0.05/1,000 gal	$ 1.37/1,000 gal[c]
Projected oil recovery credit[d]	$5.30/1,000 gal	$5.30/1,000 gal	$ 5.30/1,000 gal
Projected net operating cost	$2.77/1,000 gal	$3.76/1,000 gal	$ 3.53/1,000 gal

[a]This unit chemical cost is based on cleaning the membrane after every 100,000 gal batch.
[b]Membrane replacement costs are based on a two year membrane life.
[c]Permeate from the reverse osmosis system will be used as feed to the deionized water system. Because of its superior quality (<50 μmhos conductivity), the length between resin regenerations will be significantly extended. This credit represents the savings on chemical and labor costs over a full year.
[d]Projected oil recovery credits based on 80% recovery of the incoming oil and 20¢/gal net value.

Capital and operating costs of ultrafiltration systems are strongly dependent on the specific application, capacity, and type of system. The literature has identified many applications where UF has been effectively and economically applied. General economic advantages of systems have been given as lower chemical costs, low pretreatment costs (depending on configuration), lower energy costs since the main energy input required is to operate pumps, and lower labour requirements for operation. As well, there are economic benefits from oil recovery. The main operating costs of UF are associated with membrane replacement and cleaning.

3.2.3 Applications in the Oilfield

Studies examining the application of ultrafiltration systems to the treatment of oily wastewater associated with oil production have been limited to date. Contact with various research agencies, and the literature review revealed that little research is being conducted in this area. Generally, the relatively small size of most UF systems in current use, lack of applications experience and problems identified with membrane fouling have been factors discouraging oilfield applications. The Alberta Oil Sands Technology and Research Authority (AOSTRA) has undertaken studies examining the use of ultrafiltration for oilfield produced waters, however results have not been published in the open literature. Energy, Mines and Resources Canada has undertaken research investigating ultrafiltration of in-situ generated bitumen emulsions. The feasibility of using porous membranes to dewater and break bitumen oil/water emulsions was shown by Farnand and Poirier (1983). They tested several membranes and found that the

emulsion apeared to break on the surface of the membrane. Cellulose membranes were found to foul the least and were considered most attractive due to their hydrophilic nature. The study identified the potential suitability of other hydrophilic ultrafiltration membranes for use in treating such emulsions. The study found, however, that static test cells exhibited low permeation rates due to a build up of a polarized layer on the surface of the cell.

The static studies were followed up by tests using a continuous process (Farnand, Coulombe, and Sawatsky, 1984, and Nader, Farnand and Sawatsky, 1984). They confirmed that the use of a continuous membrane process to break these emulsions is feasible and they identified a polar material in the permeate which was considered to be the stabilizing agent. The main concern was identified to be membrane fouling, which was related to membrane material used.

Ultrafiltration has been examined for treatment of emulsions from simulated micellar-flood wastewaters by the U.S. Department of Energy (Dubey et al, 1981). These were complex wastewaters containing oil, as well as surfactants, alcohols, and polymers, that were introduced to the formation during micellar flooding. Synthetic wastewaters were prepared to simulate micellar flood waters, containing fixed levels of brine, polymer and butanol, with oil-sulphonate concentrations ranging from 400-3400 mg/L. Operating pressures were 20-40 psi (138-276 kPa) and temperatures ranged from 21-32°C (70-90 °F). Depending on oil concentration, flux rates of cellulosic membranes ranged from 20-40 gal/ft^2/day after 180 min, and the permeate was essentially free of all oils, sulphonate, and polymer. Polymeric membranes were also tested, and the researchers

found that both cellulosic and polymeric membranes produced permeates relatively free of oil sulphonate or polymer, although the cellulosic was said to provide better flux rate and was easier to clean when fouled. This study also identified the potential of ultrafiltration for treating produced waters which are destined for subsurface disposal or reinjection, since significant amounts of emulsified oil could result in formation plugging and the associated production problems. The study concluded that ultrafiltration was effective, but that further studies on actual wastewaters were necessary due to their complex and site specific characteristics.

Ultrafiltration has also been investigated for recovery of surfactant from oilfield emulsions (Baddour, 1977). The patent claimed that further concentrating ultrafiltration permeates and concentrates by membrane processes resulted in an efficient and economical process for recovering surfactant for subsequent reuse in the oilfield.

The literature has shown the wide range of UF industrial applications which have proven its technical and economical efficiency. Operating experience has shown that the advantages of UF, as compared to other conventional chemical and mechanical processes, are the effective concentration and recovery of oil, elimination of oily sludge disposed problems, a consistent and high oil removal efficiency which is virtually unaffected by feed concentration (up to the point where the emulsion breaks), and the low pretreatment and chemical requirements.

In addition to removal and concentration of oil as a step in boiler feedwater preparation, ultrafiltration may be utilized in

several other applications in the oilfield. UF may be used as a polishing step in conventional boiler feedwater treatment processes for removal of residual levels of suspended solids, turbidity and oil. As well, UF may economically provide the less rigorous treatment necessary prior to deep well disposal of produced waters to prevent formation clogging. Research has also shown that surfactants may be recovered through concentration by membranes and reinjected for recovery operations.

Ultrafiltration permeate may also be further polished by Reverse Osmosis in order to meet boiler feedwater requirements, as discussed in the following section.

3.3 Preparation of Boiler Feedwater by Reverse Osmosis

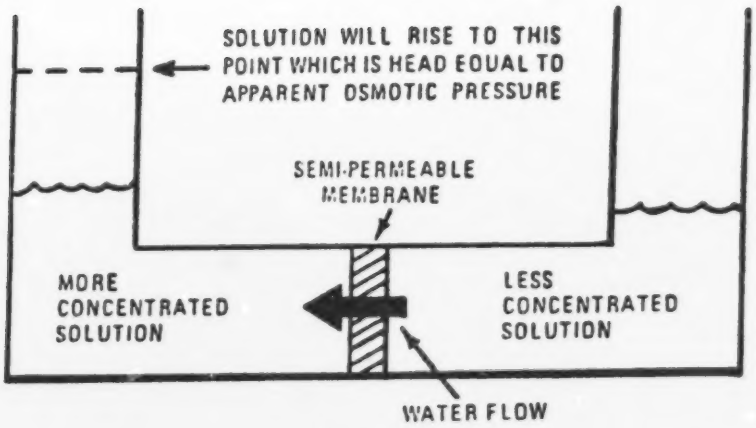
3.3.1 Process Description

As shown in Figure 3-3, osmosis is the spontaneous passage of water through a semi-permeable membrane from a less concentrated solution to more concentrated solution until equilibrium is reached. The liquid head developed at the equilibrium point is defined as the "Osmotic Pressure" (about 1 psi or 6.9 kPa per 100 mg/L total dissolved solids for water). Reverse Osmosis occurs when an applied pressure exceeding the Osmotic pressure is applied on the concentrated solution and the passage of pure water is reversed travelling from the more concentrated solution to the less concentrated solution.

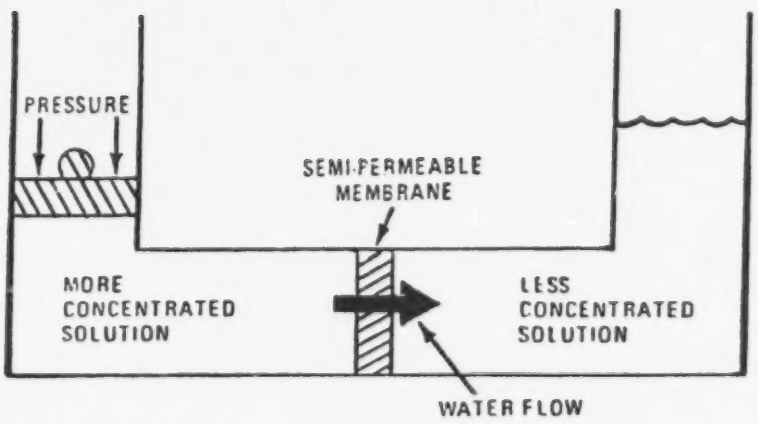
In reverse osmosis systems, the feedwater is passed across the membrane surface under turbulent flow and high pressure conditions. As the stream flows across the membrane, pressure forces pure water through the membrane. The impurities in the feedwater are

FIGURE 3 - 3

REVERSE OSMOSIS


SOLUTION WILL RISE TO THIS POINT WHICH IS HEAD EQUAL TO APPARENT OSMOTIC PRESSURE
SEMI-PERMEABLE MEMBRANE
MORE CONCENTRATED SOLUTION
LESS CONCENTRATED SOLUTION
WATER FLOW

OSMOSIS



REVERSE OSMOSIS

concentrated and carried out of the unit. Reverse Osmosis employs an anisotropic membrane with an asymmetric structure consisting of a 0.1 to 0.5 micron thick dense layer (active surface), supported by a 25 to 100 micron thick substructure.

Reverse osmosis systems are operated at a higher pressure than UF. Membrane pore sizes are smaller (5 - 50 Å), and the two mechanisms of separation are ionic salt separation and organic separation. Ionic salt separation is due to the dielectric interaction and interfacial tension effects at the water-membrane interface. The higher the charge the greater the rejection or repulsion from the surface layer. As a result of this repulsion a pure water layer sets up on the membrane surface and extends into the pore structure of the membrane. Divalent ions are rejected to a greater extent (96-99%) than monovalent ions (94-96%).

Organic separation is based primarily on the shape and size of the molecule and its relationship to location at pore sites since no pure water layer is established on the membrane surface. Extensive research has been conducted investigating the separation of various organic compounds by membrane processes (Matsuusa and Sourirajan, 1973 a and 1973 b; Dickson et al, 1975). Generally, organics with a molecular weight greater than 300 are rejected almost completely, with typical percentage rejections typically ranging from 90-99.9%, depending on the charge, molecular size, interaction forces, configuration and degree of dissociation.

In designing Reverse Osmosis systems, the feed water source and the final desired water quality are the main criteria in selecting

the type of system for a particular application. Reverse Osmosis is a modular process, allowing for accurate scale-up from pilot processes.

Operating pressures can vary from 200 to 1000 psi (1380-6900 kPa) depending on the osmotic pressure of the feedwater. For example seawater with 14,000 mg/L of total dissolved solids (TDS) has an osmotic pressure of approximately 350 psi (2415 kPa) and city water, with 200 mg/L of TDS has an osmotic pressure of about 5 psi (35 kPa). The effective applied pressure is the pressure applied minus the osmotic pressure. For seawater and brackish water, the osmotic pressure plays an important role in determining the operating pressure. In processing of typical surface water the osmotic pressure is only a small factor.

3.3.1.1 Membrane Materials

The selection of a reverse osmosis membrane system to treat produced water is based primarily on the composition of the de-oiled feedwater and the quality of the product water required. Boiler feedwater treatment requirements were described in section 2.2, and these criteria set the objectives for development of the reverse osmosis membrane process for this application.

Table 3-7 presents a summary of commercially available reverse osmosis membranes. These may be classified as cellulosic and non-cellulosic membranes. Non-cellulosic membranes give better organic rejection than cellulosic membranes. However generally, cellulosic membranes are less expensive and are more productive in terms of flux rates. The most commonly used membranes are cellulose acetate and thin-film-composite.

TABLE 3-7

COMMERCIAL REVERSE OSMOSIS MEMBRANES

Membrane Material	Configuration	Salt Separation (%)	Permeate Rate ($Lm^{-2}d^{-1}$)	Pressure (kPa)	pH (range)	Max. Temp. °C
Cellulose Acetate	Spiral	90-99	300-1000	2900-7200	4-7	25-35
	Capillary	97	200	2900	6-8	35
	Flat	<99	400	4000	2-8	30-40
	Tubular	90-98	450-700	4000	3-8	30-45
Co-Polyacrylonitrile	Flat/Tubular	95-98	1000-3000	5000-10000	1-10	45
LP-Polyamide	Spiral	96	1000	1400	2-11	35
Piperazine/ Polyepiiodohydrin/ Isophthaloyl Chloride	Spiral	>99	700	4000	4-12	40
Polyamide	Capillary	95-98.5	40-50	2900-5800	4-11	35
Polyamide TFC	Spiral	96-98	750	7200	2-10	45
Polybenzimidazolone	Spiral	>97	1000	10000	1-12	60
p-Phenylenediamine/ Trimesoyl Chloride	Flat	98	1800	4100	2-11	<60
Polysulfone, sulfonated	Capillary	N/A	N/A	N/A	2-13	70

(adopted from Pusch and Walch, 1982)

Thin-film-composite (TFC) reverse osmosis membranes are composed of two separate layers. The first layer is a thin barrier layer which performs the water and salt separation and may be formed from any of a number of membrane materials. The second layer is a microporous sublayer which supports the barrier layer. Both conventional and thinfilm composite membranes also have a third layer, a fibrous web, which serves as a back-up for the microporous support.

For each type of membrane selected there will be associated operating limitations; most Reverse Osmosis membranes have operating temperature limits of approximately 35-40°C (95-104°F) although some have been developed for conditions of up to 60°C. As well, cellulose acetate membranes have a relatively narrow pH range, whereas non-cellulosics are capable of operation at a much wider range of pH. Applied pressures also vary; for example the maximum pressure for cellulose acetate, polyamide, and TFC are 500 psi, 800 psi, and 1000 psi respectively.

The literature has revealed extensive variability in the concentration of inorganic species in produced water, therefore preliminary testing must be done in order to evaluate membrane suitability, and to determine associated operating conditions, and required pressures.

3.3.1.2 Configurations

Various configurations of Reverse Osmosis membranes are available, and as in ultrafiltration applications, are selected based on economics and operating conditions which are determined by feedwater characteristics. RO membranes are available in spiral,

tubular, and capillary configurations similar to these which were described in detail in section 3.2.1.2 for ultrafiltration, and similar operating limitations apply. In contrast to ultrafiltration, there is a wide body of experience in the operation of large-scale RO capillary systems.

For RO systems, additional pretreatment is often required to soften the feedwater. Depending on feedwater hardness levels, this may be necessary to prevent precipitation or scale formation on the membranes.

3.3.2 Current Applications and Economic Evaluation

Reverse osmosis has been sucessfully used in treating a variety of waters and wastewaters for industrial and municipal use, and has been accepted as a pretreatment step for demineralization, as well as for recycling process water at zero discharge plants (Strauss, 1981). Large scale reverse osmosis plants treating up to several million gallons per day are currently operational.

Reverse osmosis has been used to demineralize a variety of waters from low salinity municipal water to high salinity brackish and seawater to produce water for drinking, boiler feed, industrial, pharmaceutical, and medical uses. Pretreatment is often required to lower the pH (to less than 6.5 with cellulose acetate membranes) and reduce suspended solids for certain configurations. Post treatment with a second stage RO or demineralizers to reduce the soluble ions to the required levels may also be implemented, depending on product water requirements.

Reverse osmosis has proven to be efficient and economical for treatment of metal finishing wastewaters (Franza, 1981). The systems are used for purification of process waters for recycle, and recovery and reuse of the chemical concentrate. The application of membrane technology to power generation waste was discussed by Tang and Chu, (1981) and Dhwan and Doiel (1983), and considered efficient and economical. Total dissolved solids in power plant wastes were reported by Dhwan and Doiel (1983) to have been reduced by 95%, and silica reduction was in the order of 98%.

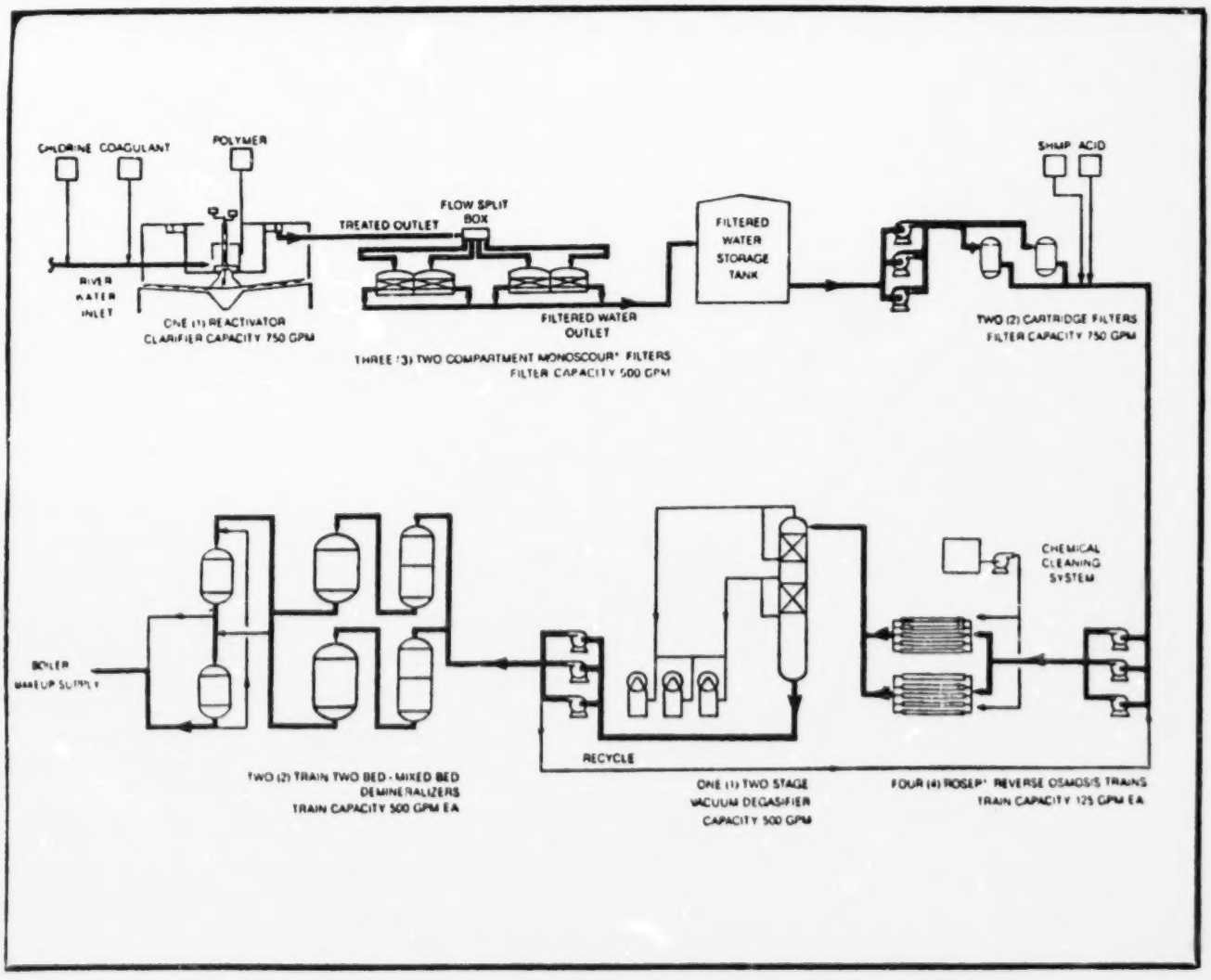
Reverse osmosis has been used in treating various waters for boiler feed water use in combination with some pre-treatment and post-treatment (Anonymous, 1976). O'Brien and LaTerra, (1981) reported on operating experience with six large reverse osmosis plants ranging in size from 450,000 GPD to several million GPD. Five of the case histories utilized the process for utility boiler make-up systems, while one was producing ultra-pure water. The feed contained total dissolved solids levels ranging from one hundred mg/L to as high as several thousand mg/L. One system was successfully handling 700,000 gallons per day of feedwater containing up to 5,000 mg/L TDS from a tidal river source. A spiral wound cellulose acetate system was with final demineralization by ion exchange. The treatment schematic is illustrated in Figure 3-4 . Projected salt rejection after 3 years operation was 91.9%.

In another system, regulatory guidelines required that a utility was to find an alternate water source to the well it was currently using. The high TDS feedwater levels (2,000 mg/L) obtained from the alternative man-made reservoir were too high to utilize in

FIGURE 3 - 4

PROCESS SCHEMATIC FOR RO TREATMENT SYSTEM ON HIGH TDS FEEDWATER

(from O'Brian and LaTerra, 1981)


CHLORINE
COAGULANT
POLYMER
RIVER WATER INLET
ONE (1) REACTIVATOR CLARIFIER CAPACITY 750 GPM
TREATED OUTLET
FLOW SPLIT BOX
FILTERED WATER OUTLET
THREE (3) TWO COMPARTMENT MONOSCOUR® FILTERS FILTER CAPACITY 500 GPM
FILTERED WATER STORAGE TANK
SHMP
ACID
TWO (2) CARTRIDGE FILTERS FILTER CAPACITY 750 GPM
BOILER MAKEUP SUPPLY
TWO (2) TRAIN TWO BED - MIXED BED DEMINERALIZERS TRAIN CAPACITY 500 GPM EA
RECYCLE
ONE (1) TWO STAGE VACUUM DEGASIFIER CAPACITY 500 GPM
CHEMICAL CLEANING SYSTEM
FOUR (4) ROSE® REVERSE OSMOSIS TRAINS TRAIN CAPACITY 125 GPM EA

the existing ion exchange plant. For the spiral wound cellulose acetate system pre-treatment consisted of clarification and filtration, and optional post treatment demineralization. After six months operations the plant was still rejecting 96% of the salt, and just experiencing a first flux decline.

Another large plant treating over 1 MGD of high TDS water for boiler make-up utilizes clarification and filtration as pre-treatment and demineralization post treatment similar to that shown in Figure 3-4. This plant identified the operational advantages of adding a scale inhibitor, such as sodium hexametaphosphate to the system. In summary, the plants examined in the study were operating reliably and cost-effectively, and potential for further expansion and application of the technology was forseen.

The ability of Reverse Osmosis to handle extremely high levels of dissolved solids has been illustrated by various installations converting seawater to potable water or for boiler feed. An example is the National Electric Company of Venezuela, where a two-stage RO has been successfully treating seawaters containing an average of 36,000 mg/L of T.D.S. (Vera, 1981). Pre-treatment was required to remove suspended solids and organic matter to protect membrane modules. The capital cost of pre-treatment constituted approximately 18% of the total system capital cost, with the Reverse Osmosis System constituting 56%. Other costs were associated with piping controls and electrical materials. The RO process was found to increase the length of time between regenerations of an ion exchange demineralization unit, through which RO product water is processed prior to entering high pressure (2,500 psi or 17250 kPa) boilers.

One of the world's largest seawater desalting facilities, utilizing reverse osmosis to produce water for steam generators for enhanced oil recovery was constructed in 1979. The system consisted of nine RO units with a total capacity of 3.6 million gallons per day and was constructed to provide feedwater for generators in steamflood operations adjacent to the Caspian sea (Leitner, 1979). Although operating data was not provided the hollow fine fiber systems were expected to remove 98.5% of dissolved solids from the seawater. The system was compared to distillation technology, and considered to be more economical due to low energy needs and lower maintenance costs. The pre-treatment utilized was acid, polyelectrolyte, and bisulfite addition, followed by sand filtration, sodium hexametaphosphate addition, and cartridge filtration. Post-treatment was not required.

The literature has illustrated the well documented technical efficiency of reverse osmosis for treatment of waters containing extremely high levels of TDS, as well as for removal of organic compounds, and the resultant production of a water quality suitable for boiler feedwater, process recycling, or potable use. The cost of RO systems are difficult to compare due to the extreme variability in feedwater quality and associated operating pressures which are required.

The capital cost for RO is also dependent on the quality of feedwater, size of system, pre and post-treatment, and membrane configuration. As with UF systems tubular configurations are often several more times expensive than spiral systems as a result of the lower membrane surface area to system volume ratio. RO has been implemented in numerous large scale industrial applications treating

up to several million gallons per day. The economic advantage of RO have been credited as their mechanical simplicity, low energy requirements and low chemical and maintenance cost. As in UF, the main operating costs are membrane replacement and cleaning.

3.3.3 Applications in the Oilfield

The potential for the application of reverse osmosis for boiler feedwater preparation has been identified by the oil industry. Reverse osmosis has been evaluated for a limited number of oilfield produced water applications, although systems have not yet been commissioned.

Previous discussion in section 2.3.2 showed that at Cold Lake, reverse osmosis was one system evaluated. However, economics at that time favoured the conventional processes. AOSTRA has sponsored some research into the application of reverse osmosis for treatment of in-situ produced water, but results have not been published and are unavailable to-date. One published study by the U.S. Department of Energy (Hicks and Liang, 1981) was conducted to determine the feasibility of reverse osmosis for treatment of oil shale processing wastewater steams. Although water composition varies from that of in-situ/heavy oil operations, especially with regard to organic composition in retort waters, some waste streams are directed to steam generation and similar treatment objectives were required. The study found that reverse osmosis was successful in treating retort waters to a water quality suitable for reuse within the plant, with TDS and organic reductions from 93-99%.

Reverse osmosis has shown to be economically competitive with the more conventional systems utilized in industrial processes. Advantages of RO have been cited as lower operating and chemical costs, lower energy requirements since the only energy required is to run the pumps, and mechanical simplicity. It is now a well established technology and large systems treating several million gallons per day are common. RO has also been utilized prior to ion exchange and has served to increase the life of the resins. It also removes dissolved organics that could normally foul the resin.

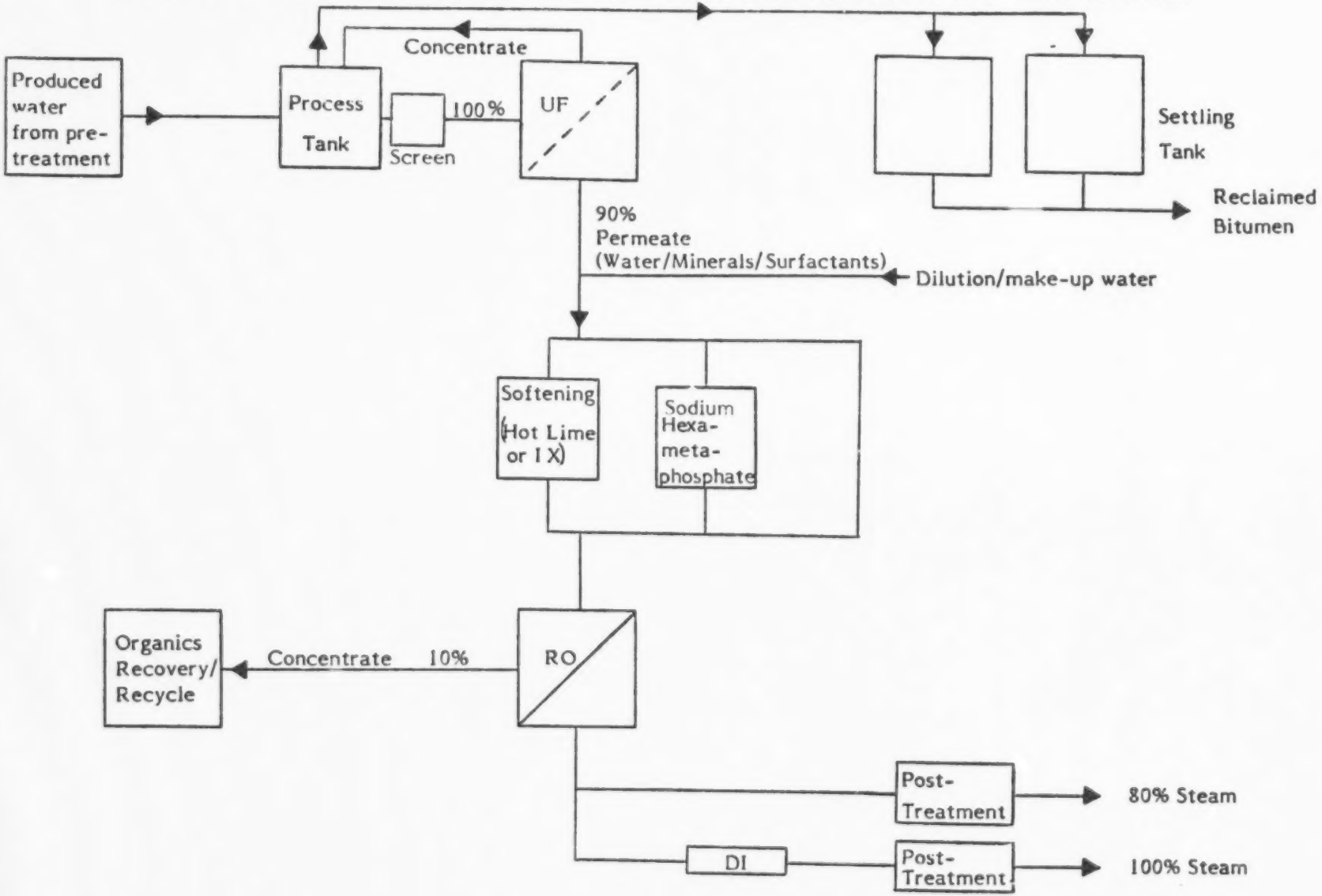
The potential for reverse osmosis in oilfield applications for boiler feedwater treatment has therefore been illustrated, however, little published information exists on actual laboratory or field evaluation. Most RO systems have been installed primarily to reduce total dissolved solids levels. Since the main treatment concern in recycling produced water for use as boiler feed water is usually the reduction of hardness levels, the potentional of RO has often been overlooked. The use of membrane technologies for treatment and recycling of produced waters has the ability to not only reduce hardness, but may result in a water quality better than that required by conventional oil-field steam generators, thus offering the potential for assessment of alternative and more efficient steam generation technologies.

3.4 Potential UF/RO Membrane System Design

Based on the literature review and related applications several schematics using membrane technology to treat produced water for steam generation can be envisaged. Figure 3-5 shows the type of

FIGURE 3 - 5.

PRE AND POST TREATMENT OPTIONS ON A UF/RO SYSTEM FOR TREATMENT OF PRODUCED WATER



possible pre and post treatment processes that may be employed to meet oil recovery and boiler feedwater objectives.

The design of a treatment system employing UF/RO processes is dependent upon numerous factors. These include feedwater composition, treatment requirements, and operating limitations of the membranes and configurations used. Prior to any UF system for oil removal, free or floating oil must be removed, usually by some form of gravity separation such as a skim or surge tank. Systems employing spiral configurations usually have stringent pre-treatment requirement, and may require filtration for the removal of all particulate matter greater than 5 microns in size. After primary oil removal, the feedwater would then flow to a process tank for flow equalization, and subsequently through the UF system. Concentrate could be recycled back to the process tank, and floating oil removed for bitumen recovery.

The addition of low-salinity, oil-free, make-up water between the UF and RO stages can also be envisioned for oilfield use to provide sufficient volume for boiler feeds. The diluted or undiluted ultrafiltration permeate could be pretreated by softening or pH adjustment if necessary prior to RO. If the RO permeate required further treatment to meet boiler feedwater objectives, ion exchange could be utilized. Post treatment includes oxygen scavenging and pH adjustment as required. Since such a system may well be capable of producing water quality better than that required for conventional steam generators, the potential exists for producing a quality suitable for 100% steam generators with deionization post treatment as necessary.

4.0 PROPOSED EXPERIMENTAL PROGRAM

The literature review has revealed the extensive variability in chemical characteristics of produced waters from heavy oil/in-situ bitumen operations. As a result treatability or evaluation test musts be conducted on specific waters to determine membrane process efficiencies. Testing determines the degree of species separation, product water quantity per square foot of membrane surface, and the recovery (ie ratio of product flow to feed flow) which can be obtained.

4.1 Recommended Membranes

Based on the discussions in previous sections and typical produced water quality as obtained from the literature, the following membranes are presented as the most promising for treatment of oil/water emulsions in heavy oil/in-situ produced water:

i) cellulose/cellulose acetate (C/CA)

ii) sulfonated polysulfone (SPS)

iii) polyvinyl difluoride (PVDF)

iv) thin film composite (TFC) (polyamide)

v) polysulfone (PS)

All of the above membranes are commercially available except for the cellulose membrane. Cellulose acetate has been proven in numerous oil/water applications, but has pH and temperature limitations and is prone to bacterial attack. Therefore the newly developed cellulose membranes, which have the advantage of a wider operating pH, will be evaluated. Both PVDF and the polyamide TFC are

very hydrophilic and offer a very wide operating range of pH and temperature conditions. They are generally resistant to bacterial and solvent attack. The membranes selected above would allow testing at a wide range of pH and temperature conditions.

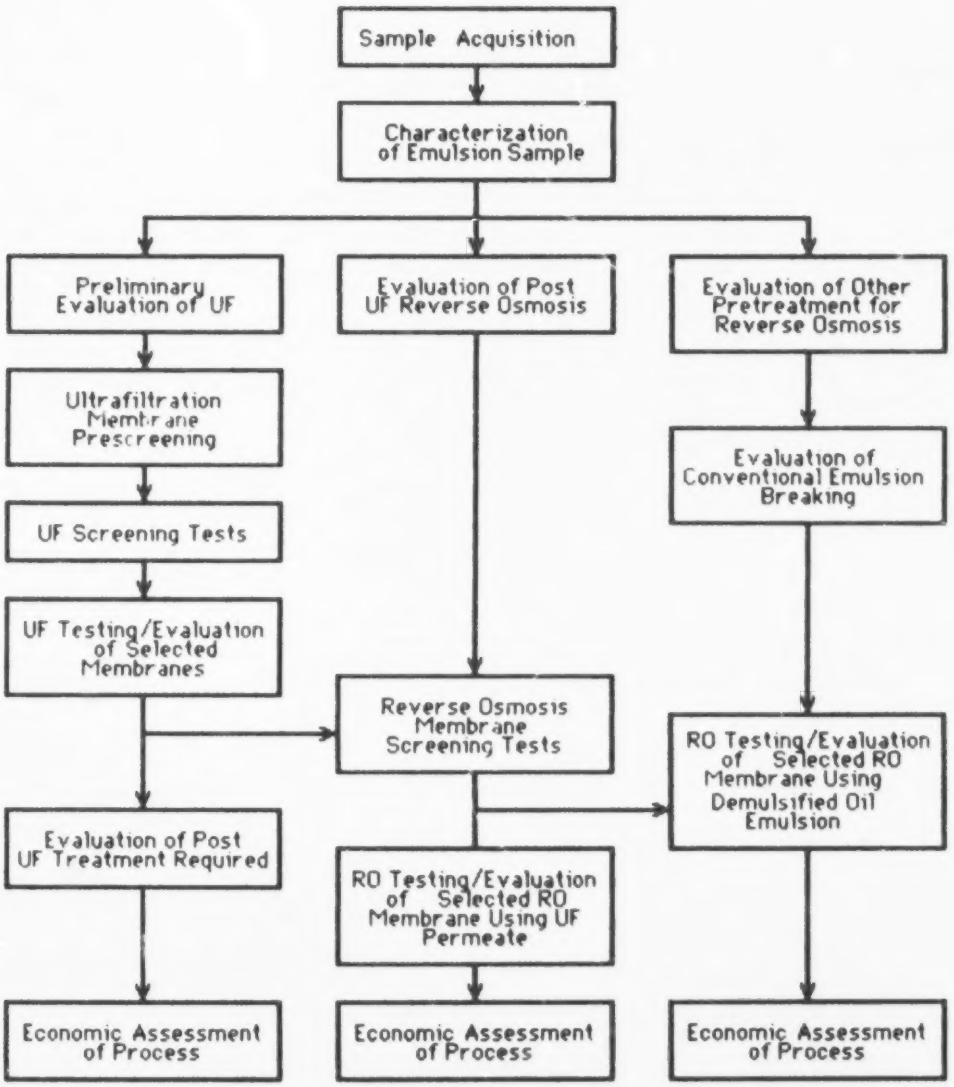
4.2 Experimental Procedures

A flow chart outlining the procedure for proposed work evaluating membranes and other treatment processes is shown as Figure 4-1. The analytical results from characterization of the produced water samples will assist in the determination of optimal UF membranes and membrane configurations as well as pretreatment requirements for UF. Membrane prescreening tests should be conducted to identify the optimum porosity of each membrane type being tested. Screening tests on optimum membranes will then identify the best membranes and operating conditions. Testing and evaluation of the best membranes should then be conducted to determine the quality of permeate and the flux rates which can be obtained under actual membrane system operating conditions. Post-treatment steps required for UF permeate to achieve boiler feed water quality should be assessed.

The analyses of ultrafiltration permeate will be used to determine the osmotic pressure and thereby assist in identifying the operating conditions and recovery limitations for subsequent reverse osmosis treatment. Reverse osmosis tests should be conducted using permeate from one of the selected UF membranes to identify the best RO membrane for use in this application and to evaluate permeate quality and flux rates under actual membrane operating conditions.

Figure 4 - 1

PROCEDURE FOR MEMBRANE AND PROCESS EVALUATIONS


Sample Acquisition
Characterization of Emulsion Sample
Preliminary Evaluation of UF
Evaluation of Post UF Reverse Osmosis
Evaluation of Other Pretreatment for Reverse Osmosis
Ultrafiltration Membrane Prescreening
Evaluation of Conventional Emulsion Breaking
UF Screening Tests
UF Testing/Evaluation of Selected Membranes
Reverse Osmosis Membrane Screening Tests
RO Testing/Evaluation of Selected RO Membrane Using Demulsified Oil Emulsion
Evaluation of Post UF Treatment Required
RO Testing/Evaluation of Selected RO Membrane Using UF Permeate
Economic Assessment of Process
Economic Assessment of Process
Economic Assessment of Process

Evaluation of conventional emulsion breaking as a pretreatment for RO and membrane tests on this broken emulsion should be conducted to assess the appropriateness of this technology.

Economic assessments should be conducted using experimental data to evaluate the costs associated with each process.

REFERENCES

Anonymous, 1976. Reverse Osmosis for Boiler Feedwater Treatment. Power Engineering, 80 (12), pp. 58-60.

Baddour, R.F., 1978. Recovering Surfactant. U.S. Patent No. 4,111,812.

Barbour, F.A. and Guffey, F.D., 1979. Organic and Inorganic Analysis of Constituents in Water produced during in-situ combustion experiements for the recovery of Tar Sands. Proceedings of the Analysis of Water Associated with Alternate Field Production Symposium, ASTM D-19 Committee on Water, Pittsburgh, Pennsylvania.

Behie L.A., Van Ham, C.J.M., and Berk, D. 1982. An Experimental Investigation into the Induced Air Flotation of Fine Oil in Water Emulsions. Proceedings of the 17th Canadian Symposium on Water Pollution Research March 1, 1982.

Bitter, J.G.A., and Reynhout, M.J., 1980 Process and Plant for Breaking of Water-Oil Emulsions. European Pat. Applic. 17,283.

Broughman, G.L., 1978. Synthetic Fuels Data Handbook, 2nd Ed. Cameron Engineers Inc.

Card, R., and Kus, J., 1983. Process Design for the Re-Use of Wastewater for Oil Production. Presented at Alberta Oil Sands Technology and Research Authority's Fourth Annual "Advances in Petroleum Technology" Conference. Calgary, Alberta, May 1983.

Carrell, M.A., 1979. Reclaiming Produced Water for Steam Generation in the Kern River Field. Paper presented at the 54th Annual Fall Technical Conference and Exhibition of the Society of Petroleum Engineers of AIME held in Las Vegas Nevada, September 23-26 1979.

Christensen, E.R., anad Plauman, K.W., 1981. Waste Re-Use: Ultrafiltration of Industrial and Municipal Wastewaters. JWPCF, 53 (7).

Churchill, R.J., 1980. Economic Considerations in Oily Wastewater Treatment. Proc. 41st International Water Conference, Pittsburg, P.A.

CH_2M-HILL Ltd., 1981. Review of Treatment and Recycling of Produced Water from Heavy Oil Fields, prepared for U.S. and Canadian Government Bodies.

CH_2M HILL, 1982. Generation of Steam Using Low-Grade Fuels and Field Produced Water for In-Situ Oil Recovery. Report prepared for Energy, Mines, and Resources, Canada.

REFERENCES (CONT'D)

Davis, J.S., Young, W.W., and Lyons, C.J., 1981. Use of Solid Fuel Possible for Field Steam Generation. Oil and Gas Journal June 8, P. 129.

Dick, 1982. Ultrafiltration for Oily Wastewater Treatment. Lubrication Engineering, 38, 4, p. 219.

Dhawan, G.K., 1978. Treatment and Recovery of Emulsified Oil by Ultrafiltration. Proceedings of the 25th Ontario Industrial Waste Conference.

Dhawan, G.K., and Doiel, R., 1983. Zero Discharge Industrial Wastewater Treatment at a T.D. Nixon Power Plant. UOP Inc., Fluid Systems Division Publication.

Dickson, J.M., Matsuura, T., Blais, P., and Sourirajan, S., 1975. Reverse Osmosis Separations of Some Organic and Inorganic Solutes in Aqueous Solutions Using Aromatic Polyamide Membranes. Journ. App. Polymer. Sci., 19, p. 801.

Dubey, S., Perez, N.L., Ramakrishnan, Bs., and Thompson, R.E., 1981. Membrane Ultrafiltration of Sulfonates and Oil from Micellar Flooding wastewaters. Prepared for U.S. Department of Energy, Report DOE / EV / 05596 - T1.

Farnand, J.R., 1981. The Treatment of Heavy Oil Emulsions with Short Chain Polar Additives. National Research Council, Division of Chemistry, Confidential Report.

Farnand, J.R., 1983. Breaking Oil-in-Water Emulsions. Canadian Patent 1148 834.

Farnand, B.A., Coulombe, S., and Sawatsky, H., 1984. Production of Boiler Feed Quality Water from Bitumen/Heavy Oil - Water Emulsion by Ultrafiltration. CANMET Division Report ERP/ERL J,OP Energy, Mines and Resources, Canada.

Farnand, B.A., and Pourier, M.A., 1983. Private Communication.

Franza, M.E., and Wilmoth, R., 1981. Evaluation of the Use of Reverse Osmosis in the Metal Finishing Industry. CENTEC (Ft. Lauderdale, FL.) Publication.

Gewers, C.W.W. 1968. Colloidal and Surface Chemical Problems in Non-Conventional Heavy Oil Recovery. Jour. of Canadian Petroleum Technology 7 (2) pp. 85-90.

Goldsmith, R.L., Roberts, D.A., and Burre, D.L., 1974. Ultrafiltration of Soluble Oil Wastes. Journ. WPCF, 46, (9) p. 2183.

REFERENCES (CONT'D)

Hayward, M.F., and Choate, W.T., 1982. Spiral Ultrafiltration: Effective Pre-treatment for Reverse Osmosis Desalination. Proced. 43rd International Water Conference, Pitts. Pennsylvania.

Hicks, R.E., and Liang, L., 1981. A Study of Reverse Osmosis for Treating Oil Shale In-Situ Wastewaters. Prepared for U.S. Department of Energy, Report DOE / LC / 10089 - T1.

Hrudey, S.E. and Scott, J.D., 1981. Water Re-Use Needs of the Oil Sands Industry in Alberta. Proc. Water Re-Use Symp. II. Am. Water Works Assoc. Res. Found., Vol. 3 1979.

Imperial Oil Ltd., 1978. Environmental Impact Statement on the Cold Lake Project. Alberta Energy Resources Conservation Board application no. 770966.

Koehler, P.B., 1983. Ultrafiltration: Treatment of Industrial Effluents for Product Recovery. Proceedings of the 30th Ontario Industrial Waste Conference.

Konak, A.R., and Grisard, P.J., 1980. Deoiling of Produced Water by Acidification. Techn. Meeting Petroleum Section CIMM, Calgary, May 25-28. Paper No. 80-31-30.

Kutowy, O., Thayer, W.L., Capes, C.E. and Sourirajan, S., 1981. Tubular Cellulose Acetate Reverse Osmosis Membranes for Treatment of Oily Wastewaters. Ind. Eng. Chem. Prod. Res. Dev., 20, p. 354.

Leitner, G.F., 1979. Caspian Seawater Treated for Solvent Project. Pet. Eng. Int'l., 51, (13) p. 64.

Lopez, C.X. and Johnston, R., 1977. Industrial Wastewater Recycling with Ultrafiltration and Reverse Osmosis. Proceedings of the 32nd Industrial Waste Conference, held at Purdue University, Lafayett Indiana.

Luthy, R.G., Sellek, R.E., and Galloway, T.R., 1978. Removal of Emulsified Oil with Organic Coagulants and Dissolved Air Flotation. JWPCF Feburary 1978, pp. 331-346.

Majid, A., and Farnand, J.R., 1980. Investigation of Norcen Emulsions. National Research Council, Division of Chemistry. Confidential Report.

Matsuura, T., and Sourirajan, S., 1973a. Reverse Osmosis Separation of Organic Acids in Aqueous Solutions Using Porous Cellulose Acetate Membranes. Journ. App. Polymer Sci., 17, p. 3661.

REFERENCES (CONT'D)

Matsuura, T., and Sourirajan, S., 1973b. Reverse Osmosis Separation of Hydrocarbons in Aqueous Solution Using Porous Cellulose Acetate Membranes. Journ. App. Polymer Sci., 17 p. 3683.

McCoy, D.R., Gipson, R.M., and Young, K.B., 1982. Demulsification of Bitumen Emulsions with a High Molecular Weight Mixed Alkylene Oxide Polyol. U.S. Patent 4,321,146

Meyer, R.F., and Dietzman, W.D., 1979. World Geography of Heavy Crude Oils, 1st International Conference, UNITAR, Edmonton, Alberta.

Nader, C., Farnand, B.A., and Sawatzky, H., 1984. Production of Boiler Feed Water From Wellhead Bitumen/Water/Mineral Emulsion by Using Porous Membranes. CANMET Report, ERP/ERL 84-21 (TR), Energy, Mines and Resources, Canada.

Nagendran, J., and Hrudey, S.E., 1981. Oil Recovery and Recycle Water Treatment for In-Situ Oil Sand Production. Proceedings of the 7th National Conf. Energy Environ. Am. Inst. Chem. Eng. Environ. Econ. Considerations Energy Utiliz. Ann Arbor Sci. Publ., Ann Arbor Mich., pp. 66-71.

O'Brien, M., and LaTerra., T., (1981). Operating Experience with Six Large Reverse Osmosis Plants. Proceed 42nd International Water Conference, Pitts. P.A., Engineers Society of Western Pennsylvania.

Pusch, W., and Walch, A., 1982. Synthetic Membranes - Preparation, Structure, and Application. Angewandte Chemis 21, 660-685. (International Edition in English).

Rowat, R.A., 1983. The Use of Spherical Agglomeration to Break Oil-Water Emulsions; A Preliminary Study. Report Submitted to National Research Council Canada.

Simon, D.E. II, 1975. Feedwater Quality in Modern Industrial Boilers. A. Concensus of Proper Current Operating Practices. Proc. 36th International Water Conference, Pittsburgh, P.A.

Snavely Jr., E.S., and Yarbrough, H.F., 1983. Offshore Oily-Water Separation. Jour. Petr. Tech. 35 (1) pp. 234-238.

Sonksen, M.K., Sittig, M.F., and Maziarz, E.F., 1978. Treatment of Oily Wastes by UF/RO; A Case History. Proceedings of the 33rd Industrial Waste Conference, held at Purdue University, Lafayette, Indiana.

REFERENCES (CONT'D)

Stephenson, R.K., Chen, J.C.T., and Cooke, P.E., 1983. Case Histories of Recycling Oil Field Produced Water for Enhanced (Tertiary) Oil Recovery Steamflood Operations. Proceedings of the Industrial Waste Symposia. 56th Annual Conference, Water Pollution Control Federal, Atlanta, Georgia, October 1983.

Strauss, S.D., 1981. Interest Grows in RO Water Treatment. Power February 1981, pp. 99-101.

Strickland, W.T., 1980. Laboratory Results of Cleaning Produced Water by Gas Flotation. Journal, Society of Petroleum Engineers, 20, 12, p. 175.

Sylvestor, N.D., Byeseda, J.J., 1980. Oil/Water Separaation by Induced-Air Flotation. Soc. Petr. Eng. Jour. 20 (6) pp. 579-589.

Tang, T.L.D., Boroughs, R.D., and Chu, T.Y.J., 1981. Application of Membrane Technology to Power Generation Waters. Industral Water Engineering, 18, (1) p. 18.

Tsui, T.P., McCort, D.J., 1979. Acute Toxicity of Produced Water, 1979. Report submitted to ESSO Resources Canada Ltd. and Gulf Canada Ltd.

Vera, I., 1981. Operating Experiences on a Reverse Osmosis Plant Which Converts Sea Water into Boiler Feed Water. Industrial Water Engineering Nov./Dec. 1981, pp. 22-29.

Wahl, J.R., Hayes, T.C., Kleper, M.H., and Pento S.D., 1979. Ultrafiltration for Today's Oily Wastewater: A Survey of Current Ultrafiltration Systems. Proceedings of the 34th Industrial Waste Conference, held at Purdue University, Lafayette, Indiana.

Warren, K., Undated. Produced water as Therma Drive Feedwater. Commercial Publication by C-E Natco Ltd.

Whalley, M.J., and Wilson, T.M., 1979. Water Conservation in a Steam Stimulation Project. First Int'l Conf. on Future of Heavy Crude and Tar Sands, Edmonton, Alberta.

ZENON, 1983. Analysis of Organics in Wastewater. Report to Environment Canada. (Under Contract No. OS83-00259).

ZENON, 1983. Environmental Review of Onshore Canadian Oil and Gas Drilling and Production Activities. Prepared for Environment Canada, Report EPS-3-EP-83-2.